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Exposure and Risk Assessment for Trichloroethanes. 1,1,1-Trichloroethane 1,1,2-Trichloroethane

Little (Arthur D.), Inc., Cambridge, MA

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An Exposure and Risk Assessment for Trichloroethanes

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This report assesses the risk of exposure to 1,1,1-trichloroethane and 1,1,2-trichloroethane. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in March of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of trichloroethanes in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to trichloroethanes for various subpopulations.

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AN EXPOSURE AND RISK ASSESSMENT
FOR TRICHLOROETHANES

1,1,1-Trichloroethane
1,1,2-Trichloroethane

by

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OFFICE OF WATER REGULATIONS AND STANDARDS
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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

Michael W. Slimak, Chief
Exposure Assessment Section
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Office of Water Regulations and Standards

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The Arthur D. Little, Inc. task manager for this study was Richard G. Thomas. Major contributors to this report were Melanie Byrne (Biological Effects and Biota Exposure), Diane Gilbert (Human Exposure), Muriel Goyer (Human Effects), and Melba Wood (Monitoring Data). In addition, Kate Scow did the EXAMS analysis, Elizabeth Cole provided substantial inputs to the human effects section, John Ostlund estimated dose/response for 1,1,2-trichloroethane and Jane Metzger and Nina Green edited and documented the report.

The materials balance for the trichloroethanes (Chapter 3.0) was provided by Acurex, Inc., produced under contract 68-01-6017 to the Monitoring and Data Support Division (MDSD), Office of Water Regulations and Standards (OWRS), U.S. EPA. Patricia Cruse was the task manager for Acurex, Inc.

Charles Delos, MDSD, was the project manager at EPA.

EPA PROGRAM CONSIDERATIONS[1]

1,1,1-Trichloroethane (often called methyl chloroform) is widely used as a solvent and in related applications. Concern about this chemical stems perhaps less from its toxicity (which is relatively low) than from its role in depleting ozone. The other isomer, 1,1,2-trichloroethane (occasionally called vinyl trichloride) is used primarily as a feedstock. Although it has substantial toxicity and suspected carcinogenicity, its environmental distribution is somewhat limited.

U.S. production of 1,1,1-trichloroethane in 1979 was 322,000 MT/yr, which represents somewhat less than half of worldwide production. About 68% of production was consumed domestically as a degreasing solvent (mostly for metal), and thereby released mostly to the atmosphere. Recycle and reuse was practiced to a very limited extent in this application, resulting in total degreasing use being about 16% greater than degreasing consumption. The remaining uses dissipate the chemical almost entirely to the atmosphere: 7% of production as an aerosol propellant, 7% in adhesives and coatings, and 7% in other solvent uses. Some 10% of production was exported or stockpiled. The ultimate disposition of the total domestic consumption is as follows: 84% to air, 10% to land, 4% to water or sewage, and 2% destroyed by incineration. About 80% of the chemical disposed of in sewers is volatilized before discharge.

U.S. production of 1,1,2-trichloroethane is estimated to be roughly 190,000 MT/yr. The exact quantity is the proprietary information of Dow Chemical Company, the sole producer, which captively consumes most of it as a feedstock to produce 1,1-dichloroethylene. Dow indicated that they sell a small amount, in the "low millions of pounds" (low thousands of metric tons), to various other industries. Although small quantities of 1,1,2-trichloroethane are also produced inadvertently during production of other chlorinated hydrocarbons, the quantities released to the environment during both intentional and inadvertent production appear to be negligible compared to the quantity which Dow markets to other industries. No information is available on how these "low millions of pounds" are consumed; however, under the worst case assumption that none of it is destroyed through use as a feedstock, then roughly 70-90% might be expected to be emitted to air, 10-30% disposed on land, and a few percent discharged to water, based on disposal patterns of other chlorinated ethanes and ethenes. Obtaining an independent estimate of environmental releases by comparing the levels of the 1,1,1- and 1,1,2- isomers found in urban air, then perhaps 10,000-20,000 MT/yr might be estimated to be released to the environment.

1,1,1-Trichloroethane is one of the most frequently detected organic priority pollutants in municipal and industrial wastewaters. The Effluent Guidelines Division detected it at least once in nearly all industrial categories; it was found particularly often in Mechanical Products and

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[1] Provided by Charles Delos, EPA Program Manager.

Paint & Ink, as well as in the Electrical, Pharmaceutical, Photographic, and Organics & Plastics industries. 1,1,2-Trichloroethane, on the other hand, is detected with intermediate frequency relative to other priority pollutants; it was most often found in Mechanical Products, Paint & Ink, and Petroleum Refining industries.

After discharge to surface water, both trichloroethanes tend to partition toward the atmosphere. The half-life for this process often ranges from a few hours to a few days (corresponding to a distance of perhaps a few miles to a few dozen miles). In the lower atmosphere 1,1,1-trichloroethane is quite stable, with half-life estimates ranging from one to several years. Consequently, the substance has the opportunity to diffuse to the stratosphere where it contributes to depletion of ozone. The half-life of 1,1,2-trichloroethane in the atmosphere is shorter, measured in months; ozone depletion is not a concern for this substance.

Trichloroethanes do not bind particularly tightly to soils. Consequently, in disposing of them as a solid waste, migration from the dump site can be expected to occur by volatilization or percolation, unless preventive measures are practiced. In groundwater, 1,1,1-trichloroethane might decompose (by hydrolysis) with a half-life of perhaps 6 months or longer to hydrochloric and acetic acids. Some dichloroethylene, which itself decomposes at about the same rate, may be formed. 1,1,2-Trichloroethane is expected to behave similarly in groundwater. It can be concluded that effective disposal of trichloroethanes must result in containment of the substances within the site for a time period long enough for decomposition to take place. Adsorption to a solid phase may or may not reduce decomposition with the same effectiveness that it reduces migration. If sorption were to slow both processes equally, then its overall effect would simply be to delay rather than to prevent migration.

The toxicity of 1,1,1-trichloroethane is somewhat less than most of the similar solvents. Animal tests have not shown it to be carcinogenic or teratogenic; however, the results are not considered to be conclusive. The National Cancer Institute was scheduled to complete further testing in 1981. It has been shown to be weakly mutagenic. EPA's water quality criterion for protection of human health is 18,400 μg/l. Acute toxicity to aquatic life has not been found at levels below several thousand μg/l.

The toxicity of 1,1,2-trichloroethane, on the other hand, is more substantial. Of most concern is the carcinogenicity shown in animal tests. EPA's water quality criterion for protection of human health is 6 μg/l (10^{-5} risk). In contrast to its toxicity to mammals, its toxicity to aquatic life appears to be similar to the 1,1,1- isomer.

Consistent with the trichloroethanes' tendency to partition to the atmosphere, where they are fairly stable to decomposition, most exposure is found to result from air rather than water contamination. For 1,1,1-trichloroethane, urban air sampling has indicated a mean concentration of

3.3 μg/m^3. Drinking water surveys have suggested a mean concentration in the neighborhood of 0.1 μg/l. Assuming inhalation of about 20 m^3/day and ingestion of 2 l/day, the aggregate exposure to this compound is far greater via air than via water. Although the data on food contamination is limited and unreliable, it suggests that exposure via food may be intermediate between air and drinking water. Exposure through fish is very small, however.

Exposure to the more hazardous 1,1,2- isomer is substantially less than for 1,1,1-trichloroethane. Observed levels of 1,1,2-trichloroethane in urban air average 0.12 μg/m^3. If the Cancer Assessment Group's extrapolation from animal tests were accurate, long-term exposure to such a level would represent a cancer risk of slightly greater than 10^{-6}. If representative nationwide, such a risk would represent a cancer incidence of 3-6 cases/year. For comparison, the observed total cancer incidence (from all causes) is over 800,000 cases/year. Aggregate exposure and risk via drinking water is difficult to quantify because the compound is so rarely detected in surface and groundwater.

Overall, it can be concluded from the findings that:

(1) Trichloroethanes are primarily air pollutants. Population aggregated exposure appears to be far greater via air than via surface and groundwater.

(2) Unless continuing tests show 1,1,1-trichloroethane to be carcinogenic, the concentrations generally found in air, surface water, and groundwater are not directly hazardous. The total quantities released to the environment might contribute to stratospheric ozone depletion, however.

(3) The levels of 1,1,2-trichloroethane observed in urban air might contribute very slightly to cancer risks. Its detection in surface and groundwater is, on the other hand, rare.

(4) Current levels of trichloroethanes in ambient surface waters are rarely expected to harm aquatic life.

1.0 TECHNICAL SUMMARY

The Monitoring and Data Support Division, Office of Water Regulations and Standards, the U.S. Environmental Protection Agency, is conducting an ongoing program to identify the sources of, and evaluate the exposure to, 129 priority pollutants. This report assesses the exposure to and risk associated with the two isomers of trichloroethane: 1,1,1-trichloroethane and 1,1,2-trichloroethane.

1.1 MATERIALS BALANCE

The compound 1,1,1-trichloroethane, also known as methyl chloroform, is a high-vapor-pressure organic solvent, primarily used in degreasing operations and as a component of other products. The chemical has become environmentally pervasive due to fugitive emissions during production, use, and disposal. The 1,1,2- isomer is also a high-vapor-pressure organic solvent, but it is used mostly as a feedstock intermediate. Environmental releases are relatively small compared with the 1,1,1- isomer.

1.1.1 1,1,1-Trichlorethane

Approximately 322,000 kkg of 1,1,1-trichloroethane were produced in 1979. Production of 1,1,1-trichloroethane has remained relatively stable since 1976, well below its 7-9% predicted growth rate. Total environmental release of the chemical from either the vinyl chloride or ethane production process is estimated to be 480 kkg (see Table 3.1); 81% (~390 kkg) of the total releases were discharged to POTWs. Approximately 80 kkg were emitted to air, and 9 kkg were discharged to land in 1979.

About 220,000 kkg (68% of the total produced) were consumed by degreasing operations. Such use results in 151,000 kkg of atmospheric emissions; 24,000 kkg were disposed to land, and 10,000 kkg were sent to POTWs. The remaining uses--aerosol vapor depressant, adhesives, paints, film cleaners, and leather tanning--result almost entirely in atmospheric emissions. Of the total 85,000 kkg consumed in such uses, 68,000 kkg (80% of the quantity used) were emitted to air. Only 420 kkg were disposed to land and 7 kkg were sent to POTWs.

1.1.2 1,1,2-Trichloroethane

The 1,1,2- isomer is produced in the U.S. directly or indirectly from ethylene and is also produced as a co-product in the manufacture of other chlorinated hydrocarbons. Its chief use is as a feedstock intermediate in the production of 1,1-dichloroethylene. Occasionally, it is used as a solvent for chlorinated rubber manufacture.

According to the U.S. International Trade Commission, Dow Chemical is the sole producer of 1,1,2-trichloroethane. The quantity produced is proprietary information. Approximately 180,000 kkg of 1,1,2-trichloroethane is estimated to be required for 1,1-dichloroethylene production. This estimate represents the maximum production potential and is probably high.

Environmental releases of 1,1,2-trichloroethane from 1,1-dichloroethylene manufacture are small.

Dow Chemical does sell some 1,1,2-trichloroethane as a consumer product but the quantity sold is considered proprietary information. A spokesperson from Dow estimated that "low millions of pounds" are used annually in various industries. Release of 1,1,2-trichloroethane to the environment also results from the manufacture of other chlorinated hydrocarbons. Total environmental releases are estimated to be 5,000 kkg/yr (1979).

1.2 FATE AND DISTRIBUTION IN THE ENVIRONMENT

1.2.1 Concentrations in Environmental Media

Trichloroethanes have been detected in all environmental media, including food and drinking water, widely throughout the United States. Data on levels in food are extremely limited but suggest that concentrations for the 1,1,1- isomer are in the low µg/kg range. Limited semiquantitative data on levels of the 1,1,2- isomer in fish indicate very low levels may be present in this food. No other data on levels of 1,1,2-trichloroethane in foods were available, but, given the much lower volume of environmental releases of 1,1,2-trichloroethane, it is assumed that most foods would contain negligible amounts, if any.

From semi-quantitative water concentration data, it has been estimated that about 20% of finished water supplies may contain >1 µg/l of the 1,1,1- isomer and only isolated instances of >10 µg/l exist. Data on the concentrations of the 1,1,2- isomer in water supplies are extremely limited and no meaningful estimates of average concentrations can be made; however, on the basis of a much lower volume of release of this isomer to the environment, it is thought that most drinking water supplies have negligible amounts of the 1,1,2- isomer.

Air monitoring data for the trichloroethanes indicate that 1,1,1-trichloroethane is ubiquitous. Concentrations in remote areas average about 0.5 µg/m^3 and in urban areas about 3.3 µg/m^3. It is estimated that the concentration of 1,1,2-trichloroethane in urban air is generally about 0.12 µg/m^3.

Ninety percent, or more, of sediment concentrations reported in STORET for both chemicals are less than 10 µg/kg.

1.2.2 Environmental Fate

Because of their high vapor pressures, trichloroethanes have high volatilization rates relative to those of many other organic chemicals, despite the fact that their solubilities are also quite high. The primary waterborne fate pathway for these chemicals is volatilization from surface water or soil, followed by slow photo-oxidation in the atmosphere. For both isomers, the half-life for volatilization from a 1-m deep stream is estimated to be 4-5 hours. Time to 90% loss is about 12 hours. For a 10-m deep stream, the estimated half-life increases to about 1 week and the time to 90% depletion is about 3 weeks. The distance for 90% to volatilize is up to 1700 km downstream from the discharge point.

When 1,1,2-trichloroethane in water solution was applied to a sandy soil column in the laboratory, about one-half volatilized and one-half percolated into the soil column. These results indicate that leaching and volatilization are the important fate processes for 1,1,2-trichloroethane in soil. No similar information has been found concerning 1,1,1-trichloroethane.

In laboratory studies, 1,1,1-trichloroethane was found to have a hydrolysis half-life of 6-7 months. In groundwater aquifers, where other fate processes do not operate, the compound may be degraded by this process. If behavior in the environment is similar to results of laboratory tests, it would take 1.5-2 years to degrade 90% of the original amount.

Little information was found concerning the biodegradation of the trichloroethanes. Biodegradability studies conducted in flasks in the laboratory indicated that both compounds were degraded by yeast extract and domestic wastewater inoculum. However, many other chlorinated solvents are resistant to biodegradation, even though they exhibit some biodegradation in wastewater treatment or laboratory studies.

The atmospheric lifetime of the 1,1,1- isomer is on the order of 6-10 years, long enough for global mixing and transport to the stratosphere to occur. (Stratospheric mixing and inter-hemispherical mixing occur on a time scale on the order of a year or less.) Ozone depletion up to 1.3% of total ozone, depending on continuing release of the chemical, may occur following Cl atom release by photodecomposition. The 1,1,2- isomer may be photolyzed more rapidly than the 1,1,1- isomer based on results of laboratory tests, although little information concerning 1,1,2-trichloroethane was found.

1.3 RISKS TO HUMANS

1.3.1 Human Effects

1.3.1.1 1,1,1-Trichloroethane

The compound 1,1,1-trichloroethane has a fairly low toxicity via inhalation due to rapid and almost total elimination of the compound, unchanged, via the lungs. The small amount that is metabolized (less than 5% of an inhaled dose) is converted by the liver to trichloroethanol and trichloroacetic acid and excreted in urine. Urinary clearance has an approximate half-life in man of 10-12 hours for trichloroethanol and 70-85 hours for trichloroacetic acid. Although inhalation exposure is most common, percutaneous absorption of both liquid and vapor 1,1,1-trichloroethane, as well as exposure via ingestion, has been demonstrated in humans.

In laboratory animals, acute LD_{50}'s range from 5,000 mg/kg to 12,000 mg/kg via oral administration and 75-98 g/m^3 for 3-7 hours via inhalation. Principal effects of acute exposure in laboratory animals are depression of the central nervous system and disturbances in cardiac function, including sensitization of the heart of epinephrine. In subchronic inhalation studies, monkeys, dogs, rabbits, rats and guinea pigs exposed to 15 g/m^3, 8 hours per day, 5 days per week for 6 weeks showed some leukopenia (reduction in the number of white blood cells), body weight reduction and nonspecific inflammatory changes. The liver appeared to be most susceptible to histopathological changes in guinea pigs and mice.

No adequate carcinogenicity studies are available for the determination of carcinogenic risks associated with exposure to 1,1,1-trichloroethane. In three studies, 1,1,1-trichloroethane caused no significant increase in tumor incidence in B6C3F1 mice (4010 mg/kg/day by gavage), Osborne-Mendel rats (1071 mg/kg/day by gavage) or Sprague-Dawley rats (9.5 g/m^3, 6 hours per day, 5 days per week for 12 months by inhalation); however, poor survival of test animals and insufficient duration of study rendered these data inadequate for use in an assessment of carcinogenicity. Further data on carcinogenicity and mutagenicity are extremely limited; weakly positive results were reported in one strain (TA100) of Salmonella typhimurium and in one mamalian cell transformation assay. No teratogenic effects associated with 1,1,1-trichloroethane exposure were observed in rats or mice exposed to 4.8 g/m^3 1,1,1-trichloroethane on days 6-15 of gestation.

At low inhalation exposures of 1,1,1-trichloroethane ($\leq$ 5.5 g/m^3), the primary effects in man are psychophysiologic, including dose-related impairment of perception and coordination and relatively little disturbance in body functions. At higher exposures (> 44 g/m^3) functional depression of the central nervous system leading to respiratory or cardiac failure are noted. Acute exposures to high levels of the compound (> 5.5 to < 44 g/m^3) by accidental contact or abuse, may result in transient kidney and liver dysfunction. The effects of chronic low-level exposures are not known.

1.3.1.2 1,1,2-Trichloroethane

Data concerning the toxicity, carcinogenicity, mutagenicity or teratogenicity of 1,1,2-trichloroethane are very limited or non-existent, particularly regarding adverse effects to man. However, based on the evidence available, 1,1,2-trichloroethane is considered much more toxic than the 1,1,1- isomer of trichloroethane.

Absorption of 1,1,2-trichloroethane has been demonstrated in both man and animals following inhalation exposure or dermal contact. In laboratory animals, fairly rapid excretion of 73-87% of an absorbed dose occurs via the urine, and 6-8% of the absorbed dose is expired unchanged. Major urinary metabolites in mice are S-carboxymethyl cysteine, chloroacetic acid, and thiodiacetic acid, and minor amounts of trichloroethanol and trichloroacetic acid.

The 1,1,2- isomer has been shown to cause central nervous system depression in mice and damage to the liver and kidney in mice and dogs following single intraperitoneal injections of 0.07-0.4 ml/kg. Acute exposure in man appears to be characterized by a narcotic effect on the central nervous system and eye and skin irritation, while possible kidney, lung, and gastrointestinal damage may result from long-term exposure.

Data from a study on carcinogenic effects indicated that 1,1,2-trichloroethane caused hepatocellular carcinomas and pheochromocytomas in B6C3F1 mice of both sexes at time-weighted doses of 195 and 390 mg/kg of body weight/day, 5 days per week, administered by gavage. Carcinogenicity data from a similar study with Osborne-Mendel rats were inconclusive. No adequate data regarding mutagenic or teratogenic effects associated with 1,1,2-trichloroethane exposure have been reported.

1.3.2 Exposure of Humans

1.3.2.1 1,1,1-Trichloroethane

The chemical 1,1,1-trichloroethane is globally pervasive in air and has been found in many samples of ground and surface drinking water. It has been detected in foods in the United Kingdom. Except for some limited data on levels in fish tissue, no data on concentrations in foods in the U.S. were found. Dermal absorption appears to be of concern only for a relatively small subpopulation that handles the chemical occupationally.

A typical daily urban exposure based on ingestion of contaminated water and food and inhalation of urban air is estimated to be about 40 μg/day/person. An upper limit on the population potentially exposed to these levels is about 150,000,000 people per day.

For rural dwellers, a typical exposure is five times less, 9 μg/day/person. Some 53,000,000 people per day might be exposed at this level.

Populations living near user or manufacturing sites may have exposures up to 2200 μg/day/person due to higher ambient air concentrations. The size of the exposed population cannot be estimated with reasonable accuracy.

Occupational absorption via inhalation and percutaneous routes may range up to 11,000 mg/day/person. This level may apply to some of the 130,000 employees in degreasing operations.

1.3.2.2 1,1,2-Trichloroethane

The compound 1,1,2-trichloroethane has been found in drinking water supplies. The estimated potential intake from drinking water ranges from negligible to <2 μg/day/person for the majority of the population, although it is possible that a very small subpopulation may ingest up to 600 μg/day/person. Limited air concentration data for 1,1,2-trichloroethane in urban air have been utilized to estimate an average absorption of about 1.3 μg/day/person via inhalation.

1.3.3 Risk Considerations for Humans

1.3.3.1 1,1,1-Trichloroethane

Currently available data do not indicate that this compound is carcinogenic. No positive mammalian teratogenic or mutagenic effects have been demonstrated. An acceptable daily intake (ADI) of 37.5 mg/day/person has been derived. Estimated urban and rural exposures are more than 500 to 4,000 times less than the estimated ADI. No toxic effects are expected from these exposures. Occupational exposures from 27 mg/day/person to 11,000 mg/day/person have been estimated; consequently, an estimated 130,000 persons (involved in degreasing operations) may be subject to adverse health effects.

1.3.3.2 1,1,2-Trichloroethane

An NCI study indicates that 1,1,2-trichloroethane is carcinogenic in mice but not rats and thus is a suspect carcinogen in humans.

Four risk extrapolation models were applied to the dose-reponse data obtained in animal experiments to indicate the range in the predicted number of possible lifetime excess cases of cancer that might result from chronic human exposure to 1,1,2-trichloroethane. The range of estimated risks obtained for the human exposure levels of interest is indicative of the inherent uncertainty associated with the mathematical models currently used for risk extrapolation purposes. There is presently no scientific concensus for selecting the most appropriate model for extrapolating high exposure levels utilized in animal experimentation to the much lower levels experienced by the human population. Each of the models is formulated in such a way that the curves pass through the origin; that is, there is some finite response at any dose greater than zero. This concept of no threshold is scientifically debatable, but it has been the position of some scientists and of government regulators that thresholds to carcinogens do not exist. The no-threshold theory tends to make the predicted risks obtained "conservative," meaning here, to overstate the risk.

In addition to the uncertainty associated with the choice of the mathematical model, there is large and unquantifiable uncertainty regarding extrapolating from laboratory animals to humans. The guidelines recommended by the U.S. EPA have been followed to calculate human doses theoretically equivalent in effect to the dosages utilized in animal experiments.

Bearing in mind these sources of large uncertainty, it is predicted that the number of excess cancers (above background level) during a lifetime from inhalation of 1,1,2-trichloroethane at the estimated average concentration in urban air of 0.12 $\mu g/m^3$ is 0.01 to 1 per million population exposed. There are approximately 150,000,000 persons who are urban inhabitants; thus, fewer than 150 cancers for this population are estimated to result from inhalation of 1,1,2-trichloroethane in urban air.

Drinking water concentration data are too limited to permit meaningful predictions concerning the U.S. population as a whole. However, some isolated findings of water levels of 1,1,2-trichloroethane as high as 300 µg/l are predicted to cause from 6 to 1,350 excess lifetime cancers per million population exposed. It should be emphasized that this high level of contamination in water appears to be extremely rare.

1.4 RISKS TO AQUATIC BIOTA

1.4.1 Toxic Effects

The lowest level at which adverse effects to aquatic organisms have been determined experimentally for trichloroethanes is 7.5 mg/l for barnacle larvae. The most sensitive fish species tested is the bluegill (LC_{50} is 69.7 mg/l for the 1,1,1- isomer; 40.2 mg/l for the 1,1,2- isomer). All toxicity values for fish and invertebrates were in the range 1.0 mg/l to 100 mg/l. Algae were quite resistant to trichloroethanes, as no acute effects were observed in test concentrations up to 670 mg/l.

1.4.2 Exposure of Aquatic Biota

The available monitoring data indicate that the concentrations of trichloroethanes found in the majority of samples taken from major river basins, and near production and use sites, were in the low µg/l range. The highest value for 1,1,1-trichloroethane detected downstream of a manufacturing site was 169 µg/l. Based upon reported ambient water concentrations, there is no overlap between aquatic exposure levels and known effects levels, since no acute or chronic effects are known to occur at less than 1.0 mg/l.

1.4.3 Risk Considerations for Aquatic Biota

All acute toxicity values for both trichloroethanes range from 1.0 mg/l to 100 mg/l for aquatic biota. Monitoring data indicate that ambient concentrations are in the low µg/l range. Water quality criteria for the two chemicals are not exceeded in ambient or effluent waters in the U.S. The risk to aquatic organisms is, therefore, assumed to be negligible.

2.0 INTRODUCTION

The Office of Water Regulations and Standards, Monitoring and Data Support Division, the U.S. Environmental Protection Agency, is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and estimate the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing suitable regulatory strategy for reducing the risk, if such action is indicated.

This report provides a brief, but comprehensive, summary of the production, use, distribution, fate, effects, exposure, and potential risks of 1,1,1-trichloroethane and 1,1,2-trichloroethane. The 1,1,1-isomer is more commonly produced and hence detected more often in environmental media than the 1,1,2-isomer. Consequently far more information is available concerning 1,1,1-trichloroethane and it is dealt with in far greater detail in each chapter.

The report is organized as follows:

Chapter 3.0 presents a materials balance for the trichloroethanes that considers quantities of the chemical consumed or produced in various processes, the form and amount of pollutant released to the environment, the environmental compartment initially receiving it, and, to the degree possible, the locations and timing of releases.

Chapter 4.0 describes the distribution of trichloroethanes in the environment by presenting available monitoring data for various media and by considering the physicochemical and biological fate processes that transform or transport the chemicals.

Chapter 5.0 describes the available data concerning the toxicity of trichloroethanes for humans and laboratory animals and quantifies the likely level of human exposure via major known exposure routes.

Chapter 6.0 considers toxicological effects on and exposure to biota, predominantly aquatic biota.

Chapter 7.0 compares exposure conditions for humans and other biota and with the available data on effects levels from Chapters 5.0 and 6.0 the risks presented by various exposures to the trichloroethanes are estimated.

Appendices A-C present more detailed information supporting materials balance estimates in Chapter 3.0. Appendix D discusses the procedure for estimating the volatilization rates of the trichloroethanes and Appendix E discusses in detail the atmospheric fate of the compounds.

3.0 MATERIALS BALANCE

3.1 INTRODUCTION

This chapter presents an environmental materials balance for 1,1,1-trichloroethane and 1,1,2-trichloroethane.

As matter is neither created nor destroyed in chemical transformations, the total mass of all materials entering a system equals the total mass of all materials leaving that system, excluding those materials the system accumulates or retains. From the perspective of risk analysis, a materials balance may be performed around any individual operation that places a specific population at risk (e.g., process water discharges creating groundwater contamination). An environmental materials balance, therefore, consists of a collection of materials balances, each of which is directed to a specific source and sink within the environment.

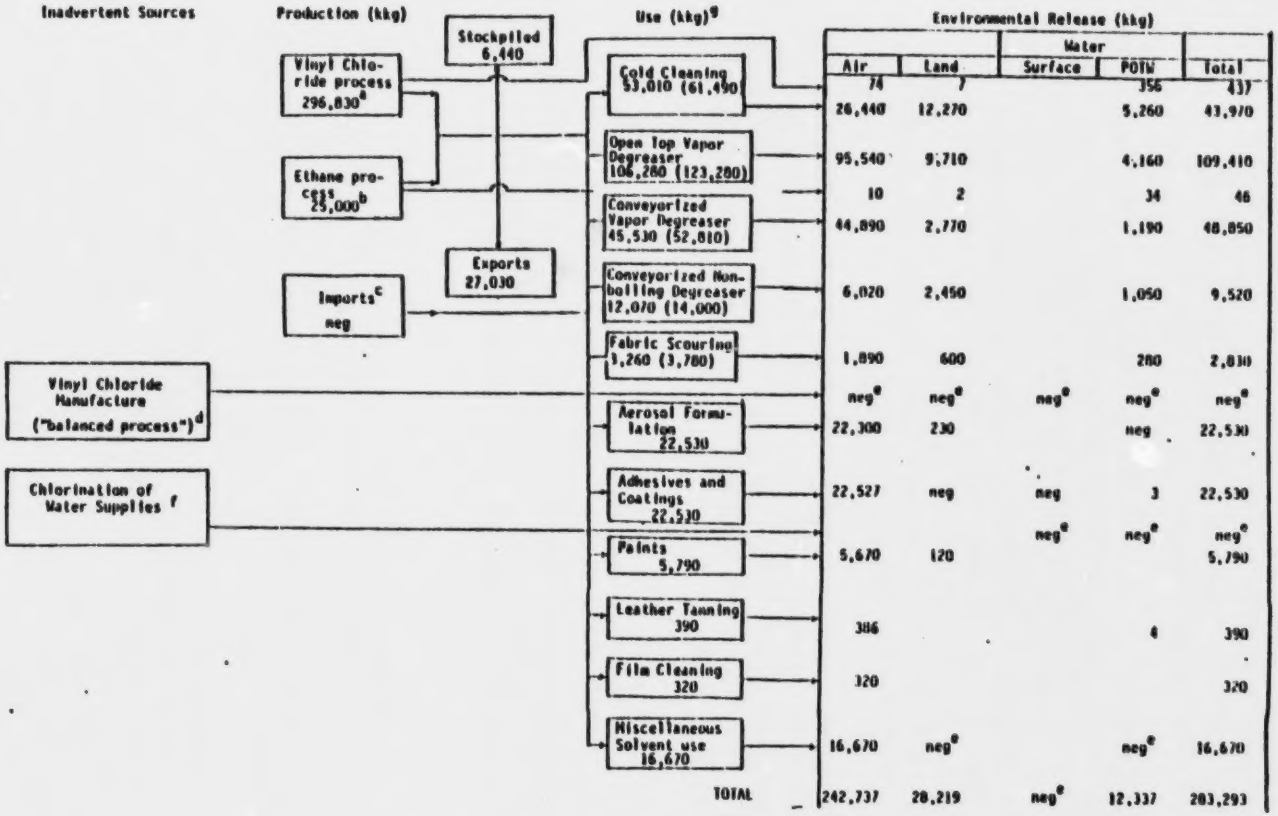
The materials balance is based on a review of both published and unpublished data concerning the production, use, and disposal of 1,1,1- and 1,1,2-trichloroethane within the United States. This data was reviewed to present an overview of major sources of environmental releases of 1,1,1- and 1,1,2-trichloroethane.

As approximately 95-99% of the 1,1,2-trichloroethane manufactured is captively consumed at the production site, major emphasis has been placed on the environmental distribution of 1,1,1-trichloroethane. Production, use, disposal, and problem areas concerning 1,1,1-trichloroethane are presented in Sections 3.3 through 3.6. Section 3.7 addresses the production, use and environmental release of 1,1,2-trichloroethane.

3.2 SUMMARY

Production of 1,1,1-trichloroethane in the U.S. has remained relatively stable since 1976, well below its 7-9% predicted growth rate and below the 12-13% growth rate exhibited between 1965 and 1974 when the compound was replacing the more hazardous trichloroethylene (Mannsville Chemical Products 1979).

The U.S. apparently produces most of the 1,1,1-trichloroethane in the world; U.S. production in 1976 totaled 2.7×10^5 kkg, while the world capacity for that year was estimated to be 4.8×10^5 kkg, 90% of which was utilized (McConnell and Schiff 1979). In 1979, the U.S. produced 321,830 kkg of the compound (Harris 1980), while the world capacity was an estimated 8.3×10^5 kkg. Of the 321,830 kkg of 1,1,1-trichloroethane produced in the U.S. in 1979, 93% (296,830 kkg) was manufactured via the vinyl chloride process, the remaining 7% (25,000 kkg) was produced by direct chlorination of ethane. As shown in Figure 3-1, 483 kkg of 1,1,1-trichloroethane were released to the environment during its production via both processes. The majority of that total released was


Inadvertent Sources
Production (kkg)
Use (kkg)[g]
Environmental Release (kkg)
Vinyl Chloride process 296,830[a]
Ethane process 25,000[b]
Imports[c] neg
Stockpiled 6,440
Exports 27,030
Vinyl Chloride Manufacture ("balanced process")[d]
Chlorination of Water Supplies[f]
Cold Cleaning 53,010 (61,490)
Open Top Vapor Degreaser 106,280 (123,280)
Conveyorized Vapor Degreaser 45,530 (52,810)
Conveyorized Non-boiling Degreaser 12,070 (14,000)
Fabric Scouring 3,260 (3,780)
Aerosol Formulation 22,530
Adhesives and Coatings 22,530
Paints 5,790
Leather Tanning 390
Film Cleaning 320
Miscellaneous Solvent use 16,670
TOTAL

	Air	Land	Water: Surface	Water: POTW	Total
	74	7		356	437
	26,440	12,270		5,260	43,970
	95,540	9,710		4,160	109,410
	10	2		34	46
	44,890	2,770		1,190	48,050
	6,020	2,450		1,050	9,520
	1,890	600		280	2,830
	neg[e]	neg[e]	neg[e]	neg[e]	neg[e]
	22,300	230		neg	22,530
	22,527	neg	neg	3	22,530
			neg[e]	neg[e]	neg[e]
	5,670	120			5,790
	386			4	390
	320				320
	16,670	neg[e]		neg[e]	16,670
TOTAL	242,737	28,219	neg[e]	12,337	283,293

Figure 3.1 Materials Balance: 1,1,1-Trichloroethane 1979 (kkg)[h]

a) See text, Section 3.3.1 for process description, Table 3.1 for environmental release derivation.

b) See text, Section 3.3.3 for process description, Table 3.2 for environmental release derivation.

c) EPA, 1979a.

d) See text, Section 3.4 for inadvertent environmental releases.

e) Negligible (<1 kkg), see Section 3.4.1.

f) See text, Section 3.4.2.

g) See Table 3.3 for environmental release calculations. Values in parentheses (for degreasing) are total solvent used, including that which is recycled; other value is virgin solvent entering the "degreasing cycle" for the first time. Environmental releases are based on the quantity of total solvent used. See Table 3.4 and Appendix C.

h) To close the materials balance, add to the total emission quantity (283,293 kkg) the amount of solvent recycled from degreasing (34,690 kkg, Table 3.2), the amount incinerated during degreasing (3,980 kkg, Table 3.2), amount stockpiled (6,440 kkg) and the amount exported (27,030 kkg). Actual production (321,830 kkg) plus the amount of solvent added to the system from previous year's degreasing recycle (35,210) totals 357,040 kkg.

Thus: 283,293 kkg + 34,690 kkg + 3,980 kkg + 6,440 kkg + 27,030 kkg = 355,433 kkg
and: 35,210 kkg + 321,830 kkg = 357,040.
Therefore: 355,433 kkg 357,040 kkg = 99.5% of the total 1,1,1-trichloroethane is accounted for.

sent to Publicly Owned Treatment Works (POTW's) (390 kkg); about 84 kkg were emitted to the atmosphere and 9 kkg were land-disposed.

The 1,1,1- isomer is used in degreasing, aerosol formulation; manufacture of adhesives, coatings, and paints; leather tanning, film cleaning and other miscellaneous solvent operations. Figure 3-1 lists quantities of the compound consumed by each use in 1979, as well as the resulting environmental releases. Of the total 282,810 kkg of 1,1,1-trichloroethane released to the environment from use of the compound, 86% (242,653 kkg) was emitted to the atmosphere, 10% (28,210 kkg) was land-disposed, and 4% (11,947 kkg) was sent to POTWs. Negligible amounts of 1,1,1-trichloroethane were discharged to surface waters.

3.3 MANUFACTURE OF 1,1,1-TRICHLOROETHANE[1]

The bulk of 1,1,1-trichloroethane production in the U.S. is based upon the vinyl chloride process; only minor amounts (≈10%) are made by the ethane process. In the vinyl chloride process, vinyl chloride reacts with hydrogen to form 1,1-dichloroethane, which is then thermally chlorinated to produce 1,1,1-trichloroethane. The yields, based on vinyl chloride, range from approximately 95% to 98%. The 1,1,1- isomer is also produced by the noncatalytic chlorination of ethane. Ethyl chloride, vinyl chloride, vinylidene chloride, and 1,1-dichloroethane are produced as by-products.

The largest releases of 1,1,1-trichloroethane to the environment during its production, by both processes, are to aquatic media. Nearly 81% (356 kkg) of the total 437 kkg of 1,1,1-trichloroethane released to the environment during production via the vinyl chloride process was discharged to water; 74% (34 kkg) of the total 46 kkg of 1,1,1-trichloroethane released from the direct chlorination process was discharged to water. Atmospheric emissions from the vinyl chloride process totaled 7 kkg while emissions from the direct chlorination process were 10 kkg. Land destined 1,1,1-trichloroethane wastes totaled 76 kkg, 74 kkg of which were attributable to the vinyl chloride process; 2 kkg were released from the direct chlorination process.

3.3.1 Vinyl Chloride Process

Figure 3-2 outlines a simplified process for production of 1,1,1-trichloroethane via vinyl chloride (see Appendix A, Note 5 and Figure B-1, Appendix B for further details). Vinyl chloride, hydrogen chloride, $FeCl_3$ catalyst, ammonia, chlorine and stabilizer compounds are introduced into the system to yield 1,1,1-trichloroethane. Wastes are generated from the following point and nonpoint sources: heavy and light end distillation column vents; miscellaneous wastewater discharges; fugitive emissions; spent catalyst filters; 1,1,1-trichloroethane column vents; product storage vents and handling operations. However, 1,1,1-trichloroethane is released to the environment from only the last five of the above

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[1] Based on the process description of EPA (1979b).

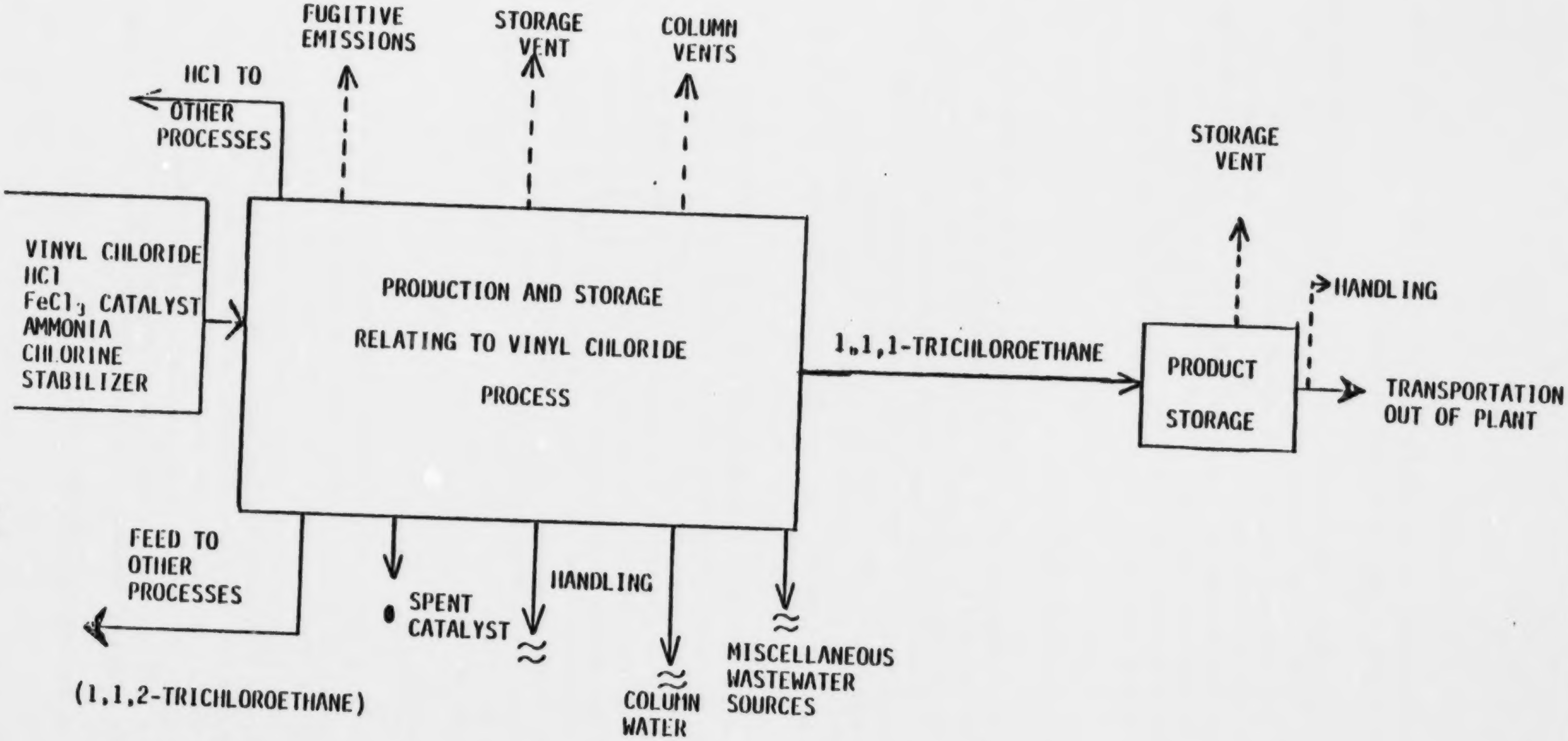
FUGITIVE EMISSIONS
STORAGE VENT
COLUMN VENTS
HCl TO OTHER PROCESSES
STORAGE VENT
VINYL CHLORIDE
HCl
FeCl$_3$ CATALYST
AMMONIA
CHLORINE
STABILIZER
PRODUCTION AND STORAGE RELATING TO VINYL CHLORIDE PROCESS
HANDLING
1,1,1-TRICHLOROETHANE
PRODUCT STORAGE
TRANSPORTATION OUT OF PLANT
FEED TO OTHER PROCESSES
(1,1,2-TRICHLOROETHANE)
● SPENT CATALYST
HANDLING
≈
≈
COLUMN WATER
≈
MISCELLANEOUS WASTEWATER SOURCES

Figure 3.2 Waste Releases from 1,1,1-Trichloroethane Production Via Vinyl Chloride Process[a]

a) ⇡ = Air emissions; ≈ = water discharge; and ● = land disposal.

Source: EPA, 1979a,b.

sources. Estimated environmental releases of 1,1,1-trichloroethane from this process are shown in Table 3-1; derivations of these estimates are given in Table B-1, Appendix B.

3.3.2 Environmental Releases from the Vinyl Chloride Process

As shown in Table 3-1, nearly 81% (356 kkg) of the total quantity of 1,1,1-trichloroethane released to the environment from its production via the vinyl chloride process (437 kkg) was discharged to water, while approximately 17% (74 kkg) was emitted to the atmosphere and 2% (7 kkg) was land-disposed.

The majority (90%) of the 1,1,1-trichloroethane wastes discharged to water was contained in effluents from refrigerated vent condensers, which were used to control emissions from product storage and handling (EPA 1979b); liquid wastes generated from both of these sources were sent to POTWs (EPA 1979b). The remaining 35 kkg of 1,1,1-trichloroethane liquid wastes from the vinyl chloride process stem from the 1,1,1-trichloroethane column (vent TC, Figure B-1, Appendix B) and were also discharged to POTWs.

Approximately 74 kkg of 1,1,1-trichloroethane were emitted to the atmosphere during its production by the vinyl chloride process (Table 3-1). Nearly 80% (58 kkg) of these wastes came from product storage and handling. The remaining atmospheric emissions (Tables 3-1 and B-1, Appendix B) were a result of 1,1,1-trichloroethane column losses (4 kkg) and fugitive emissions (12 kkg).

Only 7 kkg of 1,1,1-trichloroethane wastes (2% of the total wastes) were disposed to land. This waste was a semisolid spent catalyst complex ($NH_4 \cdot FeCl_3 \cdot NH_3$) composed primarily of 1,1,1-trichloroethane (EPA 1979b).

3.3.3 Chlorination of Ethane

The compound 1,1,1-trichloroethane is also produced by direct chlorination of ethane; small amounts of 1,2-dichloroethane and 1,1,2-trichloroethane are produced as by-products. To maximize 1,1,1-trichloroethane production, ethyl chloride and 1,1-dichloroethane are recycled to the chlorination reactor; vinyl chloride and vinylidene chloride are catalytically hydrochlorinated to 1,1,-dichloroethane and 1,1,1-trichloroethane, respectively.

$$H_2C = CHCl + HCl \xrightarrow{FeCl_3} CH_3CHCl_2$$

$$CH_2 = CCl_2 + HCl \xrightarrow{FeCl_3} CH_3CCl_3$$

TABLE 3-1 ENVIRONMENTAL RELEASES OF 1,1,1-TRICHLOROETHANE DURING PRODUCTION BY THE VINYL CHLORIDE PROCESS, 1979 (kkg)

Producer (location)	Quantity Produced (10^3 kkg)[b]	Estimated Environmental Releases[a]			
		Air[c]	Land[d]	Water[e]	Total
Dow Chemical Co. (Freeport, TX)	122	31	3	153	187
Dow Chemical Co. (Plaquemine, LA)	80	20	2	100	122
PPG Industries, Inc. (Lake Charles, LA)	95	23	2	103	128
Total	297	74	7	356	437

a) Control devices and their removal efficiencies are: product storage and handling (refrigerated vent condensers--85%); 1,1,1-trichloroethane vent (aqueous scrubber/recycle--90%). See Appendix A for emission factors used.

b) Quantity of 1,1,1-trichloroethane produced from vinyl chloride process (297,000 kkg) = total quantity produced minus quantity produced by the direct chlorination of ethane (Harris 1980; Philips 1980).

c) Product storage and handling account for >75%.

d) Waste composed of spent catalyst complex.

e) Product storage and handling account for >85%.

Source EPA (1979a,b).

Figure 3-3 represents a simplified process flow diagram for production of 1,1,1-trichloroethane via direct chlorination of ethane (see also Figure B-2). Ethane, chlorine, stabilizer, $FeCl_3$ catalyst and ammonia are introduced into the system to yield 1,1,1-trichloroethane. During the process, wastes are generated from the following point and nonpoint sources: fugitive emissions; distillation column vents; recycle and product storage vents; spent catalyst filters; handling operations; quench column vents; and miscellaneous wastewater sources. Wastes containing 1,1,1-trichloroethane are released to the environment from only some of the aforementioned sources, specifically: fugitive emissions; 1,1,1-trichloroethane distillation column; recycle and product storage vents and handling operations. Table 3-2 (and Table B-2 in Appendix B) summarizes the estimated environmental releases of 1,1,1-trichloroethane from this process.

3.3.4 Environmental Releases from the Direct Chlorination Process

Approximately 74% (34 kkg) of the total 1,1,1-trichloroethane (46 kkg) released to the environment during its production by the direct chlorination of ethane was discharged to water, 21% (10 kkg) was emitted to air, and 4% (2 kkg) was disposed to land (Table 3-2; see Table B-2, Appendix B).

All of the 1,1,1-trichloroethane discharged to water during its production via direct chlorination was contained in effluents from refrigerated vent condensers used to control emissions from recycle storage vents, product storage vents and handling (EPA 1979b). Liquid wastes from these sources were sent to POTWs (EPA 1979b).

Approximately 10 kkg of 1,1,1-trichloroethane were emitted to the atmosphere during its production via the direct chlorination of ethane (Table 3-2, see Table B-2, Appendix B). All of this waste came from the recycle storage vent, product storage vent and handling (EPA 1979b).

Only 2 kkg of 1,1,1-trichloroethane were land-disposed. This waste was captured by the glycol pot control devices used on the 1,1,1-trichloroethane column vents; see Figure B-2, Appendix B for vent locations (EPA 1979b).

3.4 INADVERTENT SOURCES OF 1,1,1-TRICHLOROETHANE

Certain industrial processes not directly related to 1,1,1-trichloroethane production generate 1,1,1-trichloroethane-containing wastes, which are annually released to the environment in small quantities (i.e., <1 kkg).

3.4.1 Vinyl Chloride Manufacture

Virtually all vinyl capacity in the United States (≈95%) is based upon the "balanced process," which incorporates direct and oxy-chlorination

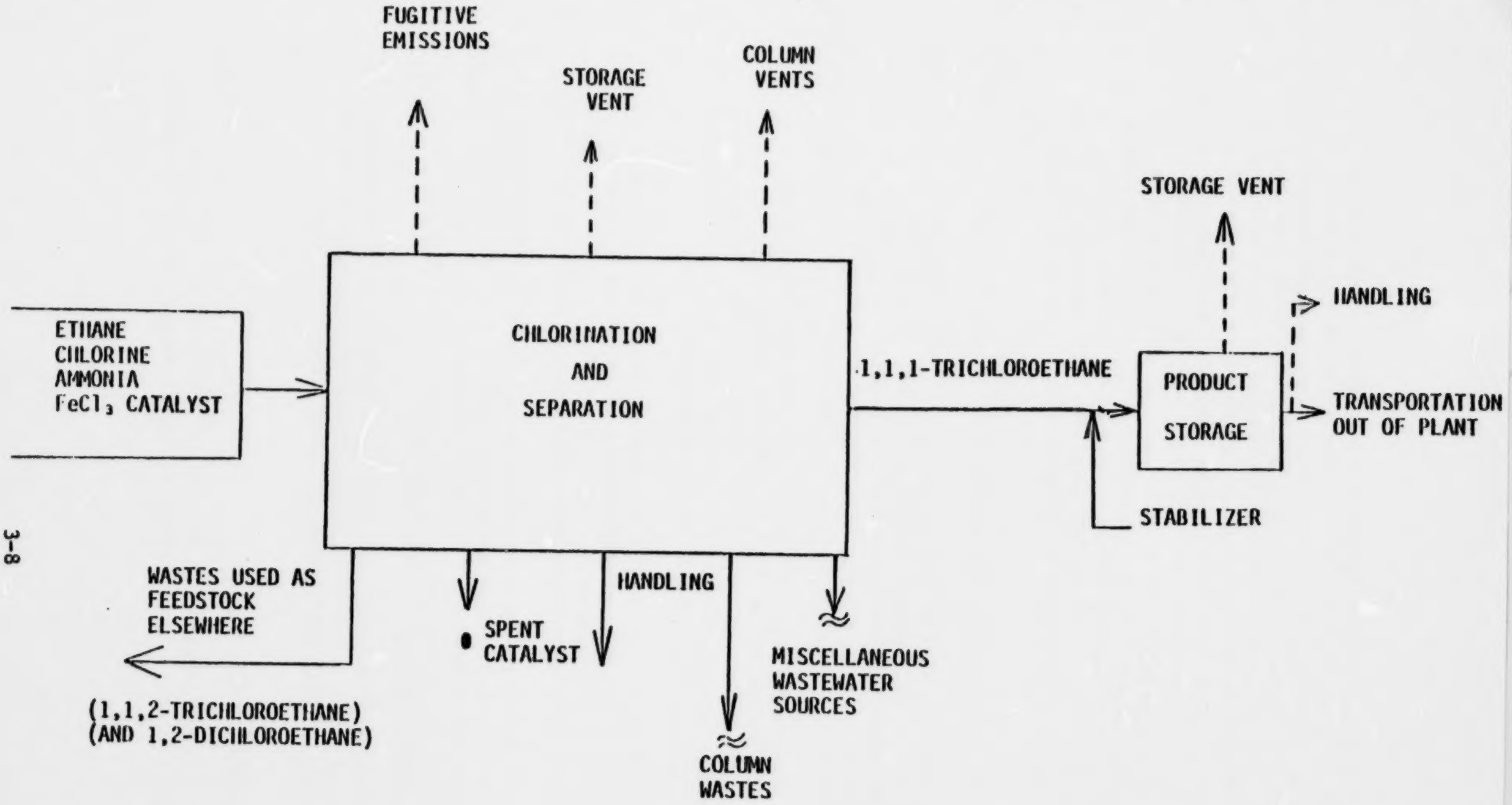
FUGITIVE EMISSIONS
STORAGE VENT
COLUMN VENTS
ETHANE
CHLORINE
AMMONIA
FeCl₃ CATALYST
CHLORINATION AND SEPARATION
1,1,1-TRICHLOROETHANE
PRODUCT STORAGE
STORAGE VENT
HANDLING
TRANSPORTATION OUT OF PLANT
STABILIZER
WASTES USED AS FEEDSTOCK ELSEWHERE
(1,1,2-TRICHLOROETHANE)
(AND 1,2-DICHLOROETHANE)
SPENT CATALYST
HANDLING
MISCELLANEOUS WASTEWATER SOURCES
COLUMN WASTES

Figure 3.3 Waste Releases from 1,1,1-Trichloroethane Production Via Direct Chlorination of Ethane[a]

---

[a] ⇡ = Air emissions; ≈ = water discharge; and ● = land disposal.

Source: EPA, 1979a,b.

TABLE 3-2 ENVIRONMENTAL RELEASES OF 1,1,1-TRICHLOROETHANE DURING PRODUCTION BY THE ETHANE PROCESS, 1979 (kkg)

Producer (location)	Quantity Produced (10^3 kkg)[a]	Estimated Environmental Releases[b]			
		Air	Land	Water	Total
Vulcan (Geismar, LA)	25	10	2	34	46

a) Philips (1980).

b) Controlled releases, see Appendix A and Table B-2 in Appendix B for calculations and emission factors. Wastes emitted to air stem from storage and handling operations and fugitive emissions; land releases result from control device wastes; water discharges are a result of handling and storage operations.

Source: EPA (1979b).

of ethene (Catalytic 1979). A typical flow diagram of the "balanced process" for vinyl chloride manufacture is shown in Figure B-3 in Appendix B. Wastes containing 1,1,1-trichloroethane are generated by the three distinct aspects of the process: direct chlorination of ethene, oxy-chlorination of ethene and dehydrochlorination of 1,2-dichloroethane and are typically combined at any given facility for recovery, treatment and disposal. Therefore, the specific point sources of aqueous and solid wastes at a manufacturing site are a function of the actual engineering design and by-product production. Wastewater streams from the direct chlorination and oxy-chlorination of ethene may include: washwater from vent gas scrubbers; dichloroethane washwater; drying column wastewater; the aqueous stream from the oxy-chlorination quench area and the aqueous stream from the light-ends distillate decanter. However, 1,1,1-trichloroethane has not been detected in wastewater from these sources (EPA 1975a).

Vent gases from the direct-chlorination and oxy-chlorination processes contain nitrogen, small amounts of hydrogen chloride, chlorine, unreacted ethene, vinyl chloride, methane, ethane and carbon monoxide, but do not contain 1,1,1-trichloroethane [see Note 7, Appendix A, (EPA 1975a, McPherson et al. 1979)].

The two sources of solid wastes from vinyl chloride monomer production, heavy ends from the 1,2-dichloroethane purification column and reactor tars (see Figure B-3, Appendix B for waste source locations) both contain inadvertently-produced 1,1,1-trichloroethane. Based on 1978 quantities of vinyl chloride produced, approximately 20 to 1,140 kkg of 1,1,1-trichloroethane were contained in heavy ends wastes generated by the "balanced process" (see Appendix A, Note 8 for calculations). However, it is likely that <1 kkg of the compound is released to the environment because the heavy ends are either treated to recover organic compounds for in-house use or incinerated with a 99.9% destruction efficiency (McPherson et al. 1979).

Similarly, the tars generated by the "balanced process" contained approximately 24 kkg of 1,1,1-trichloroethane (see Appendix A, note 9 for calculations). These nonrecoverable tars are either incinerated with 99.9% destruction efficiency or disposed as solid waste to a landfill (EPA 1975a, Lunde 1965).

3.4.2 Chlorination of Water

Chlorination of municipal water supplies apparently is not an inadvertent source of 1,1,1-trichloroethane, as post-chlorination effluent levels of the compound are not consistently higher than those prior to chlorination. In fact, slightly lower concentrations were found in treated effluent waters than untreated effluent waters (EPA 1977a, EPA 1977b, Sievers et al. 1977).

3.5 USES OF 1,1,1-TRICHLOROETHANE

Use of 1,1,1-trichloroethane, one of the least toxic chlorinated hydrocarbons, had been expected to increase (almost 10%) in the past ten years and replace the more hazardous trichloroethylene. However, 1,1,1-trichloroethane has captured only an estimated 25% of the vapor degreasing market (Mannsville Chemical Products 1979). Table 3-3 lists consumption quantities and estimated environmental releases of 1,1,1-trichloroethane from its use in degreasing, aerosol formulation, adhesives manufacture, and other smaller volume uses. Use quantities are based on the 1978 use distribution pattern and industry trends (EPA 1979a, Mannsville Chemical Products 1979).

3.5.1 Degreasing Operations

Degreasing is the removal of oils, fats, grease and wax from metals, glass, plastics, and textiles by an organic solvent. The 1,1,1-isomer is particurlarly suitable for degreasing due to its nonflammability, relatively low toxicity and medium solvency. The basic types of degreasing operations and estimated environmental releases of 1,1,1-trichloroethane from such operations are presented in Table 3-4.

Of the total 220,130 kkg of 1,1,1-trichloroethane (virgin solvent, see Appendix C) used in degreasing, 53,010 kkg were utilized in cold cleaning, 106,280 kkg in open top vapor degreasing, 57,600 in conveyorized degreasing and 3,260 kkg in fabric scouring. Table B-4, Appendix B, lists various industries that employ some form of these operations.

3.5.2 Cold Cleaning

Two types of cold cleaning are performed: maintenance degreasing, used primarily in automotive and general plant cleaning, and manufacturing cleaning, usually associated with metal working. About 137,400 facilities employ 1,1,1-trichloroethane in cold cleaning operations (EPA 1979c). The geographic distribution of cold cleaning operations is shown in Figure 3-4. In both maintenance and manufacturing cold cleaning, the parts to be cleaned are sprayed, soaked or brushed with solvent. Depending upon the specific operation, the parts are loaded and unloaded manually or mechanically (conveyorized) into the degreaser (see Table 3-4). Environmental releases of 1,1,1-trichloroethane from cold cleaning are delineated in Table 3-4. By far, most of the 1,1,1-trichloroethane lost to the environment from cold cleaning is emitted to the atmosphere; in 1979, emissions totaled 26,440 kkg. Approximately 12,270 kkg were released to land, and 5,260 kkg were sent to POTWs. An estimated 15,770 kkg of the total 1,1,1-trichloroethane were waste solvent load recycled (EPA 1979c).

Table 3.3 Use of 1,1,1-Trichloroethane and Estimated Environmental Releases, 1979 (kkg)

		Estimated Environmental Releases			
e	Quantity Consumed	Air	Land	Water	Total
greasing (total)[a]	220,130	174,780	27,860	11,940	214,580
Cold cleaning (total)	53,010	26,440	12,270	5,260	43,970
Manufacturing	23,310	11,630	4,730	2,030	18,390
Maintenance	29,700	14,810	7,540	3,230	25,580
Open-top vapor degreasing	106,280	95,540	9,710	4,160	109,410
Conveyorized vapor degreasing	45,530	44,890	2,770	1,190	48,850
Conveyorized nonboiling degreasing	12,070	6,020	2,450	1,050	9,520
Fabric scouring	3,260	1,896	660	280	2,830
rosol formulation[b]	22,530	22,300	230	neg	22,530
hesvies and coatings[c]	22,530	22,527	neg	3	22,530
her	23,170				
Paints[d]	5,790	5,670	120		5,790
ilm cleaner[e]	320	320		neg	320
eather tanning[f]	390	386		4	390
iscellaneous solvent use[g]	16,670	16,670	neg	neg	16,670
orts[h]	27,030				
ckpiled[i]	6,440				
Total	321,830	242,653	28,210	11,947	282,810

Based on EPA emission factors and solvent waste and recovery factors. Quantity consumed for degreasing includes only virgin solvent, environmental releases include those from recycled solvent. See Table 3.2 and Appendix C.

Based on 99% of solvent evaporating from product dispersion; the remaining 1% is left in container and sent to landfills (Anthony, 1980; Simmons, 1980). Negligible is defined as <1 kkg.

Table 3.3 (concluded).

c) Based on effluent data from EPA "paragraph 8" Recommendation Package for the Adhesives and Sealants Industry, 1979e. Total industry-wide untreated discharge of 1,1,1-trichloroethane is projected to be 2,920 kg per year. Of the 1,500 known adhesives and sealant facilities, only seven are direct dischargers. Therefore, the quantity of 1,1,1-trichloroethane being directly discharged is negligible. Less than 33% of the indirect dischargers provide treatment. The total quantity discharged is 3 kkg per year. See Appendix A, Note 10.

d) Based on 98% of the 1,1,1-trichloroethane used evaporating as product is used, the remaining 2% is landfilled as machinery cleaning residue (EPA, 1979b).

e) Film cleaning is a manual operation (applied by hand) with no emission control device; all 1,1,1-trichloroethane used is evaporated.

f) Based on 99% lost to atmosphere, see text (Lollar, 1980, EPA, 1979a).

g) Miscellaneous solvent uses assumed to result entirely in atmospheric emissions, see text. Miscellaneous uses include pharmaceutical extraction solvent and lubricant in cutting oils or metal drilling and tapping.

h) Harris, 1980.

i) Based on difference in production and sales in 1978, extrapolated to 1979, USITC, 1979.

j) Water discharges include both discharges to POTWs and discharges to ambient waters.

Table 3.4 Estimated Environmental Releases of 1,1,1-Trichloroethane from Degreasing Operations, 1979 (kkg)

Degreasing Operation	Total Quantity Consumed[a]	Virgin Solvent Used[a]	% Solvent Wasted (average) and Total Waste Solvent Load[b]		Quantity Recycled[c]	Estimated Environmental Releases: Air[d]	Land[e]	Water[e] Surface POTW	Total
Cold cleaning:									
Manufacturing	27,040	23,310	40-60(50)	13,520	6,080	11,630 (8,140-15,120)	4,730	2,030	18,390
Maintenance	34,450	29,700	50-75(62.5)	21,530	9,690	14,810 (10,370-19,250)	7,540	3,230	25,580
Open-top vapor degreasing	123,280	106,280	20-25(22.5)	27,740	12,480	95,540 (66,880-124,200)	9,710	4,160	109,410
Conveyorized vapor degreasing	52,810	45,530	10-20(15)	7,920	3,560	44,890	2,770	1,190	48,850
Conveyorized nonboiling degreasing	14,000	12,070	40-60(50)	7,000	2,030	6,020 (4,210-7,830)	2,450	1,050	9,520
Fabric scouring	3,780	3,260	40-60(50)	1,890	850	1,890 (1,320-2,460)	660	280	2,830
Total[g]	255,360	220,130		79,600	34,690	174,780	27,860	11,940	214,580

---

a) Based on total production of 321,830 kkg of 1,1,1-trichloroethane (Harris, 1980) and a percentage use distribution pattern similar to that of 1978 (EPA, 1979b). Virgin solvent is that which is entering the system for the first time; total quantity consumed is virgin solvent plus that which is recycled from previous year (see Appendix C for derivation).

b) EPA, 1979c. Waste solvent is that which contains impurities from degreased parts and is distinct from vapor emissions (due to evaporation from the degreaser) or from carry-out of solvent from degreased parts.

c) Based on 45% of the total waste solvent load being reclaimed by distillation and recycled (EPA, 1977d).

Table 3.4 (concluded)

d) Based on emission of 430 g solvent/kg solvent consumed for maintenance and manufacturing cold cleaners, 775 g solvent/kg solvent consumed for open-top degreasers, 850 g solvent/kg solvent consumed for conveyorized vapor degreasing, 430 g solvent/kg solvent consumed for conveyorized nonboiling degreasers, and 500 g solvent/kg solvent consumed for fabric scourers. The range shown represents the ± 30% uncertainty of the emission factor (EPA, 1979c).

e) Based on engineering judgements: 35% of the total waste solvent load is disposed to land (dumped on grounds around facility or in landfills) and 15% to water (dumped in drains resulting in discharge to POTWs). Of the remaining solvent, 45% is recycled (often distillation) and 5% is incinerated, generating insignificant atmospheric emissions.

f) Totals may not add due to rounding.

3.5.3 Open-top Vapor Degreasing

In open-top vapor degreasing, a vapor zone is created by heating the solvent; parts to be cleaned are immersed, the solvent vapor condenses and impurities are washed away. A solvent spray is sometimes employed to assist in removing heavy soil (EPA 1979c). Open-top vapor degreasers are utilized in metal working plants for manufacturing cleaning and are also suited for degreasing of intricate electrical parts where a high degree of cleanliness is required (EPA 1977d). Geographic distribution of open-top (and conveyorized) vapor degreasers is shown in Figure 3-5. Approximately 4,000 establishments utilize 1,1,1-trichloroethane in open-top vapor degreasing (EPA 1979c).

Although the body of the open top vapor degreaser is extended to minimize the escape of solvent vapors, 87% (95,540 kkg) of the total 1,1,1-trichloroethane lost to the environment from such operations is in the form of atmospheric emissions from solvent diffusion and convection and carry-out on cleaned parts (Table 3-4). As noted in Table 3-4, 9,710 kkg of 1,1,1-trichloroethane are disposed to land from waste solvent disposal, 4,160 kkg are discharged to POTWs and 12,480 kkg of the total waste solvent load are recycled.

3.5.4 Conveyorized Vapor Degreasing

Conveyorized vapor degreasing employs the same process technique as open-top vapor degreasing except that work to be cleaned is mechanically transported to and from the degreaser. About 600 facilities employ 1,1,1-trichloroethane in conveyorized vapor degreasing (EPA 1979c); the geographic distribution of conveyorized (and open-top) vapor degreasers is shown in Figure 3-5.

Carry-out of vapor and liquid solvent is usually the largest source of solvent loss from conveyorized vapor degreasers since the units are normally enclosed except for small areas for entry and exit of material to be cleaned. Total atmospheric loss of 1,1,1-trichloroethane from conveyorized vapor degreasers, as shown in Table 3-4, is 44,890 kkg; approximately 2,770 kkg were released to land and 1,190 to POTWs. Approximately 3,560 kkg of the total 1,1,1-trichloroethane waste solvent load was recycled.

3.5.5 Fabric Scouring

A relatively small amount of 1,1,1-trichloroethane, 3,260 kkg, was consumed in fabric scouring, which is essentially conveyorized cold cleaning (see Table 3-4). The geographic distribution of fabric scouring facilities is shown in Figure 3-6.

Fabrics are scoured prior to dying and finishing to remove waxes and sizings accumulated during production. Material is fed into the degreaser where it is sprayed with solvent; multilayer treatment (several

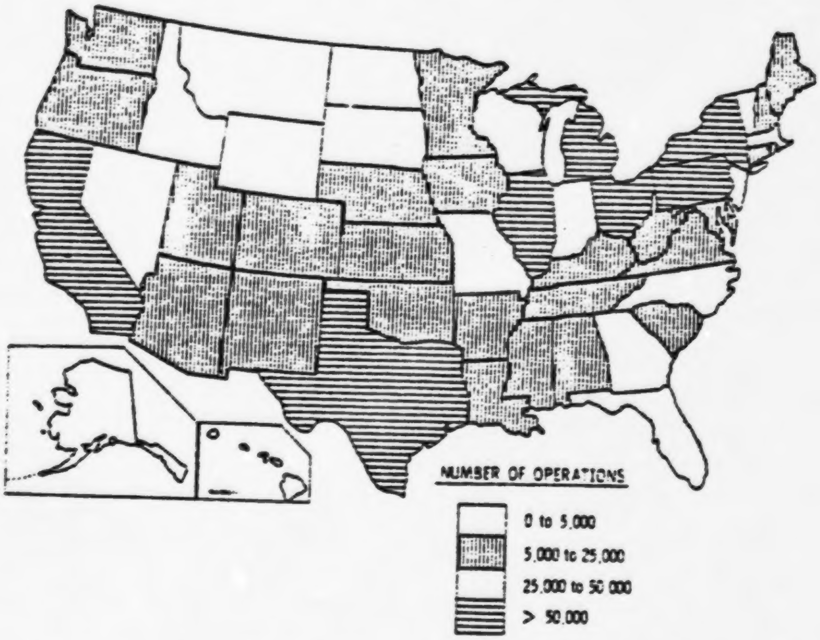
NUMBER OF OPERATIONS
0 to 5,000
5,000 to 25,000
25,000 to 50 000
> 50,000

FIGURE 3-4 GEOGRAPHIC DISTRIBUTION OF COLD CLEANING OPERATIONS

Source: EPA (1979c)

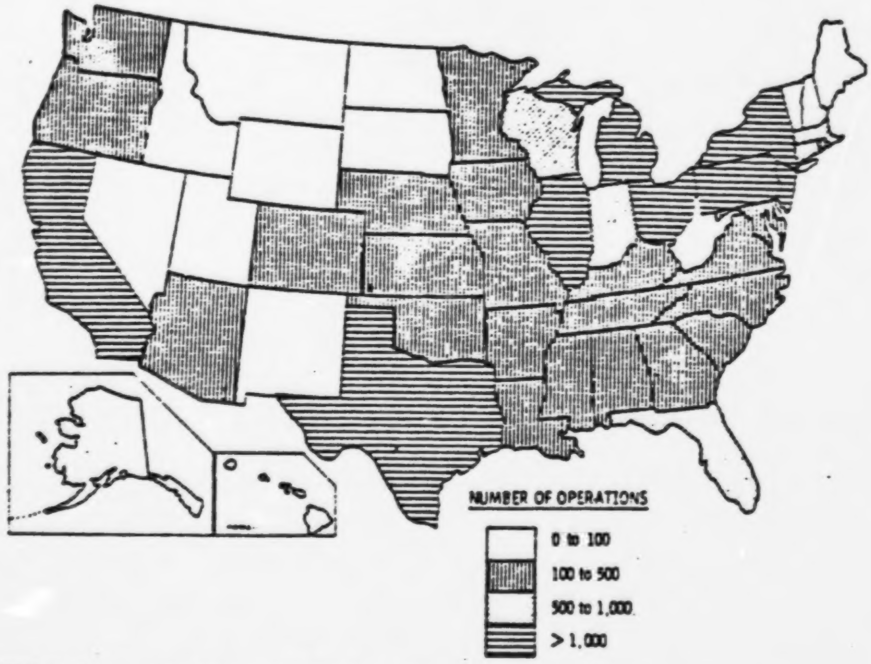
NUMBER OF OPERATIONS
0 to 100
100 to 500
500 to 1,000
> 1,000

FIGURE 3-5 GEOGRAPHIC DISTRIBUTION OF VAPOR DEGREASING OPERATIONS[a]

a) Includes open-top and conveyorized degreasers.
Source: EPA (1979c)

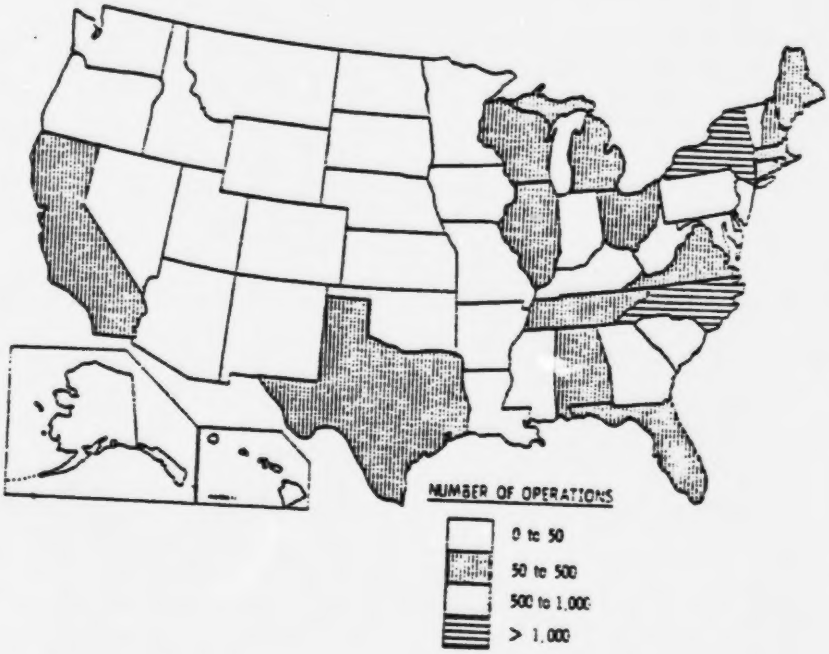
NUMBER OF OPERATIONS
0 to 50
50 to 500
500 to 1,000
> 1,000

FIGURE 3-6 GEOGRAPHIC DISTRIBUTION OF FABRIC SCOURING OPERATIONS

Source: EPA (1979c)

layers of fabric are fed through the degreaser at once) is sometimes performed to increase throughput (EPA 1979c). Table 3-4 gives environmental losses of 1,1,1-trichloroethane from fabric scouring operations; 1,890 kkg of the total 1,1,1-trichloroethane loss occurs as atmospheric emissions. Approximately 660 kkg of 1,1,1-trichloroethane were land-disposed, while 280 kkg were sent to POTWs (Table 3-4).

3.5.6 Aerosol Formulation

The quantity of 1,1,1-trichloroethane used as a solvent and vapor depressant in aerosols is not directly reported; based on SRI (1978) estimates of 18,000 kkg of 1,1,1-trichloroethane used and an expected increase in use due to the ban on chlorofluorocarbon use in aerosols, approximately 22,530 kkg of 1,1,1-trichloroethane were utilized in aerosol formulation in 1979 (Anonymous 1977; SRI 1978, EPA 1979a). The compound 1,1,1-trichloroethane is a strong candidate for replacing chlorofluorocarbons due to its flammability-suppressing nature as well as its solvency (for hair spray resins), availability, and relatively low toxicity (Anthony 1979). The compound is found in insecticide sprays, automotive cleaning products, household cleaners, and personal care items (Gordon and Hillman 1979, Hile 1977).

Losses of 1,1,1-trichloroethane from manufacturing of aerosol products occur during filling of the containers; such losses are atmospheric and total no more than 1% of the total amount of solvent consumed. Thus, approximately 230 kkg of 1,1,1-trichloroethane are emitted to the atmosphere from manufacture of aerosol products (Anthony 1980, Simmons 1980)

Approximately 22,070 kkg of 1,1,1-trichloroethane are emitted to the atmosphere from use of aerosol products, since the solvent evaporates as it is dispensed from the container. Only 1% (230 kkg) of the total 1,1,1-trichloroethane present remains in the "empty" container (Simmons 1980, Anthony 1980) and is assumed to be landfilled (Table 3-4).

3.5.7 Adhesives and Coatings

The adhesives and sealant industry, consisting of about 1,500 establishments, utilized 22,530 kkg of 1,1,1-trichloroethane in 1979 in the production of water- and solvent-based adhesives, especially contact cements (EPA 1979a, EPA 1979e, Miron 1980). Geographic distribution of the adhesive facilities is shown in Figure 3-7.

Batch blending of adhesives occurs in enclosed vessels; emissions of 1,1,1-trichloroethane are estimated to be 1% of the total solvent present, or 230 kkg (Miron 1980). The remaining emissions, 22,297 metric tons, are lost during preparation of adhesive material by spraying and 1,1,1-trichloroethane evaporation from product use (see Appendix A, Note 10).

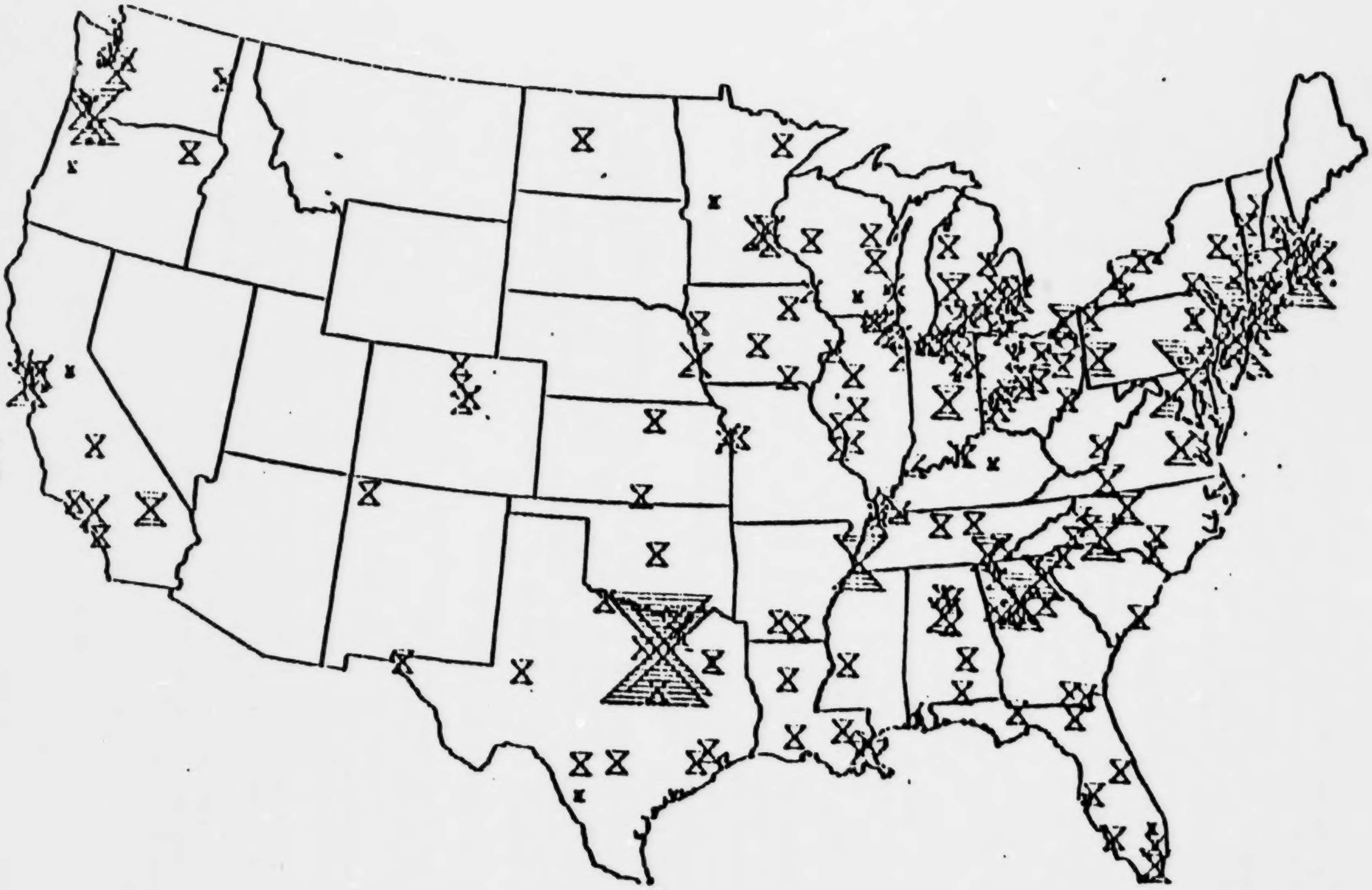

FIGURE 3-7 GEOGRAPHIC DISTRIBUTION OF THE ADHESIVES INDUSTRIES

Size of symbol (X) proportional to number of facilities.
ce: EPA (1979a)

Aqueous discharges of 1,1,1-trichloroethane are minimal; only 8 kg of this solvent are discharged industrywide per day (EPA 1979e). A maximum of 3 kkg of 1,1,1-trichloroethane would be discharged industrywide, assuming a 365 day per year operation (see Table 3-4). Of the 1,500 adhesive and sealant facilities, only seven discharge directly to surface waters; loss of 1,1,1-trichloroethane to surface waters appears to be negligible (EPA 1979e).

Use of 1,1,1-trichloroethane in the adhesives industry is being phased out, perhaps due to regulations such as Los Angeles' Rule 66. The solvent is, however, still an important component of water-based contact cements.

3.5.8 Small Volume Uses of 1,1,1-Trichloroethane

The 1,1,1-isomer is used, to a small extent, in paints, as a film cleaner, in leather tanning and other miscellaneous solvent applications (see Table 3-4). Such uses result primarily in atmospheric emissions, with less significant quantities being discharged to water. Table B-5, Appendix B lists detection frequency of 1,1,1-trichloroethane in various industrial wastewaters.

3.5.9 Paints

In 1979, approximately 5,790 kkg of 1,1,1-trichloroethane were utilized as a solvent in traffic paint formulation (EPA 1979a). Application of such paints is performed by spray equipment with no emission control devices, therefore an estimated 98% (or 5,670 kkg) of the solvent evaporates during product dispersion. The remaining 2% is left in paint containers or contained in machinery cleaning residues (120 kkg); both of these are disposed to land.

3.5.10 Film Cleaning

An estimated 320 kkg of 1,1,1-trichloroethane were used in 1979 as motion picture film cleaner; this solvent is especially suitable for this use due to its nonflammability. Since such cleaning is a manual operation, all of the solvent so used evaporates, resulting in 320 kkg of 1,1,1-trichloroethane being emitted to the atmosphere.

3.5.11 Leather Tanning

In 1979, approximately 390 kkg of 1,1,1-trichloroethane were used in the tanning industry to waterproof leather. The solvent-containing waterproofing solution is applied with a flow coater, which provides a "falling curtain" of solution over the hide as it is moved by a conveyor belt (Lollar 1980). Such systems are usually equipped with a canopy exhaust system, venting fumes to the atmosphere. An estimated 99% of the total solvent present (386 kkg) is emitted to the atmosphere as the solvent evaporates from the "falling curtain" of water proofing solution (Lollar 1980). The remaining 4 kkg are sent to POTWs. This estimate seems high since 1,1,1-trichloroethane was detected in wastewaters of only 3 out of 7 leather finishing establishments in quantities of ≤10 μg/1 (Lollar 1980, EPA 1980b).

3.5.12 Miscellaneous Small-volume Uses

Miscellaneous uses of 1,1,1-trichloroethane in pharmaceutical extraction solvents, metal cutting, drilling and tapping oils, and other non-specified solvent applications consumed an estimated 16,670 kkg in 1979. Its use as a drain and septic tank cleaner appears to have been discontinued.

Although the FDA banned the use of 1,1,1-trichloroethane in drug products in 1973 (Mannsville Chemical Products 1979), the compound has been detected in wastewaters from this industry in small amounts. Based on EPA data (see Appendix A, Note 11) <1 kkg of 1,1,1-trichloroethane is sent to POTWs annually (EPA 1980c). These aqueous discharges could stem from the use of 1,1,1-trichloroethane as an extraction solvent or from its application in equipment cleaning.

Use of 1,1,1-trichloroethane in lubricating oils for metal cutting and the unspecified solvent uses are assumed to result in atmospheric emissions. Approximately 16,670 kkg of 1,1,1-trichloroethane would be emitted to the atmosphere from miscellaneous solvent use.

In the past, 1,1,1-trichloroethane has been used as a component of drain and septic tank cleaners. Several industrial spokespersons reported that, to their knowledge, such use has been discontinued (Elliot 1980, Ashland Chemical 1980). The Consumer Product Safety Commission did not list 1,1,1-trichloroethane as a componenet of drain or septic tank cleaners as of December 1979 (Consumer Product Safety Commission 1980). Cleaning compounds containing 1,1,1-trichloroethane have, for the most part, been removed from the market (Anonymous 1979), since they have extensively contaminated groundwater in areas of Nassau County, New York.

3.6 MUNICIPAL DISPOSAL OF 1,1,1-TRICHLOROETHANE

Loading of 1,1,1-trichloroethane to POTWs is largely dependent upon variations in industrial discharges and the type of industry in a particular municipality. A framework for calculating the total 1,1,1-trichloroethane flow through the nation's POTWs is provided by data from a recent EPA study (EPA 1980c). A materials balance of 1,1,1-trichloroethane at the treatment plants can be constructed using a total nationwide POTW flow of approximately 10^{11} 1/day (EPA 1978b) and median values of 66 μg 1,1,1-trichloroethane/1 (influent) and 10.4 μg/1 (effluent) (EPA 1980c). It is assumed for purposes of these calculations that influent and effluent flow rates are equal, i.e., water loss from sludge removal and evaporation are small compared to influent flows (see Note 12, Appendix A). Using these data, approximately 2,410 kkg of 1,1,1-trichloroethane are contained in POTW influent nationwide and 380 kkg in effluent.

Approximately 4 kkg of 1,1,1-trichloroethane were contained in land-destined POTW sludge, based on a raw sludge concentration of 30.8 µg/l (EPA 1980c), and 6 x 10^6 kkg dry sludge generated per year (EPA 1979f, see Appendix A, Note 12).

The amount of 1,1,1-trichloroethane emitted to the atmosphere from POTWs can be estimated by the difference in influent, effluent and raw sludge waste loadings. Thus, 2026 kkg of 1,1,1-trichloroethane are emitted to the atmosphere from POTWs per year (Note 12, Appendix A). This estimate seems reasonable due to the volatility of the compound and aeration practices and the high temperature associated with wastewater treatment.

Some of the 1,1,1-trichloroethane entering POTWs was possibly biodegraded, but no specific data were found.

3.7 PRODUCTION AND USE OF 1,1,2-TRICHLOROETHANE

The compound 1,1,2-trichloroethane is a colorless, nonflammable liquid produced in the U.S. directly or indirectly from ethylene; it is also a coproduct in the manufacture of other chlorinated hydrocarbons. Its chief use is as a feedstock intermediate in the production of 1,1-dichloroethylene. Occasionally it is used as a solvent for chlorinated rubber manufacture (Archer 1979).

According to the U.S. International Trade Commission, Dow Chemical is the sole domestic producer of 1,1,2-trichloroethane (USITC 1979). Both USITC and Dow regard the quantity produced as proprietary information (Farber 1980). Based on a production of 122,450 kkg of 1,1-dichloroethylene, reaction stoichiometry, and an estimated 90% yield (EPA 1978), approximately 187,100 kkg of 1,1,2-trichloroethane would be required to yield the quantity of 1,1-dichloroethylene currently being produced (see Note 13, Appendix A). This estimate represents the maximum production potential and is probably high because Dow Chemical produces 1,1-dichloroethylene from either 1,1,2- or 1,1,1-trichloroethane, depending upon economics and feedstock availability (EPA 1978).

Environmental releases of 1,1,2-trichloroethane from 1,1-dichloroethylene manufacture are small; an EPA study found no 1,1,2-trichloroethane in process vent gas (EPA 1979b). Volatile organic compounds (VOC) emissions at the Dow facility are controlled by incineration and refrigerated condensers with removal efficiencies of 98 and 93%, respectively (see Table 3-5); Hedley *et al.* (1975) report no 1,1,2-trichloroethane in the 1,1-dichloroethylene separation column wastewater.

Table 3.5 Production, Use, and Estimated Environmental Dispersion of 1,1,2-Trichloroethane in 1979 (kkg)

Production	Use	Estimated Environmental Releases		
		Air	Land	Water
Chlorination of 1,2-dichloroethane 187,100[a]	Production of 1,1-dichloroethylene 187,100	neg[b]		neg[c]
1,2-dichloroethane purification		60[d]		
1,1,1-trichloroethane production, vinyl chloride process 750[f]		neg[e]	neg[e]	neg[e]
1,1,1-trichloroethane production, ethane process 1,640[f]		neg[e]	neg[e]	neg[e]
	Miscellaneous 5,000[g]	4,000	900	100

a) Based on 1,1-dichloroethylene production of 122450 kkg (EPA, 1978), 90% yield (EPA, 1978) and reaction stoichiometry.

b) Not detected in vent gas from reactors or distillation columns (EPA, 1979b).

c) Not detected in waste water streams (Hedley, et al., 1975).

d) Based on 2 kg 1,1,2-trichloroethane discharged/kkg EDC produced by direct chlorination (Hedley, *et al.*, 1975). EDC production by direct chlorination 3.08 x 10^6 kkg, and 1% of waste escaping incineration.

e) All of that which is produced (as a by-product) is recycled within the plant (EPA, 1979b).

f) See text.

g) Order of magnitude estimate of deposition of "low millions of pounds" which Dow markets to other industries, see text.

The dispersion of 1,1,2-trichloroethane to the environment also results from the manufacture of other chlorinated hydrocarbons (see Table 3-5). From manufacture of 1,2-dichloroethane by direct and oxychlorination respectively, 0.039% and 0.453% (by weight) of the process effluent is 1,1,2-trichloroethane. During purification of 1,2-dichloroethane, 2 kg of 1,1,2-trichloroethane produced by direct chlorination (Hedley et al. 1975). Based on 1978 production of 3.08 x 10^6 kkg (USITC 1979) of 1,2-dichloroethane by direct chlorination and the above discharge factor, about 6,000 kkg of 1,1,2-trichloroethane would be contained in solid wastes (see Note 14, Appendix A). These wastes are recycled as feed materials for other processes (generating no waste) or incinerated at approximately 99% efficiency. If 1% of the total solid waste generated escapes incineration, approximately 60 kkg of 1,1,2-trichloroethane would be emitted to the atmosphere (see Table 3-5).

During manufacture of 1,1,1-trichloroethane by the vinyl chloride process, 2.6 kg of 1,1,2-trichloroethane would be emitted to the atmosphere (see Table 3-5).

During manufacture of 1,1,1-trichloroethane by the vinyl chloride process, 2.6 kg of 1,1,2-trichloroethane are produced per kkg 1,1,1-trichloroethane (Elkin 1969). Based on a production of 289,700 kkg of 1,1,1-trichloroethane by the vinyl chloride process (USTIC 1980), about 750 kkg of 1,1,2-trichloroethane would be produced; usually, these heavy ends are used as feed materials for other chlorocarbons within the same plant (EPA 1979b). Approximately 51 kkg of 1,1,2-trichloroethane are produced per kkg of 1,1,1-trichloroethane manufactured by the chlorination of ethane; again all of that which is produced is recycled within the plant (EPA 1980).

Dow Chemical does sell some 1,1,2-trichloroethane as a consumer product (Dow Chemical 1980) but the quantity sold is considered proprietary information. A spokesperson from Dow estimated that "low millions of pounds" are used annually in various industries (see Table B-6, Appendix B)(Farber 1980).

For the purpose of providing approximate estimates of the uses and releases, 5000 kg/yr will be taken to be the quantity which Dow markets to other industries. Based on disposal patterns of other chlorinated ethanes and ethanes, then roughly 4000 kkg/yr might be expected to be emitted to air, less than 1000 kkg/yr disposed of on land and perhaps 100 kkg/yr discharged to water, assuming that the purchasing industries do not use it as a feedstock. These quanitites constitute the major environmental releases of 1,1,2-trichloroethane.

The 1,1,2-trichloroethane isomer has been detected in small quantities in several types of industrial wastewaters as shown in Table B-6, Appendix B (EPA 1980b). Out of 1,982 samples, the compound was found only 58 times at concentrations greater than 10 μg/l; the minimum concentration was 12 μg/l, the maximum 3,400 μg/l.

Very small quantities of 1,1,2-trichloroethane have been found in POTWs across the country (EPA 1980c). Based on a nationwide POTW flow of 10^{11} l/day (EPA 1978b) and influent and effluent concentrations of 1.9 and 0 μg/l, respectively, approximately 69 kkg of 1,1,2-trichloroethane is contained in POTW influent and zero in the effluent. The quantity of 1,1,2-trichloroethane contained in POTW sludge can be determined using a raw sludge concentration of 10.9 μg of 1,1,2-trichloroethane/l (EPA 1980c) and the quantity of dry sludge generated per year, 6×10^6 kkg. Based on these data, and assuming that wet sludge is 95% water by weight, approximately 1 kkg of 1,1,2-trichloroethane is contained in POTW sludge each year. As ocean dumping of sludge is mandated to cease by 1981, and increasing stringent air quality standards will probably curb sludge incineration, the 1 kkg of 1,1,2-trichloroethane is assumed to be land-disposed. The amount of 1,1,2-trichloroethane emitted to the atmosphere from POTWs can be estimated by differences among the quantities to the compound to influent, effluent and sludge. Thus, approximately 68 kkg of 1,1,2-trichloroethane were emitted to the atmosphere from POTW. This seems reasonable in light of the compound's volatility, and the high temperatures and aeration techniques required for water treatment. Biodegradation of the compound is a possible explanation for the difference in influent, effluent and sludge concentrations; however, no specific data were found.

Chlorination of municipal water supplies is known to produce chlorinated hydrocarbons (Sievers et al. 1977); however, it appears that such inadvertent production of 1,1,2-trichloroethane does not occur. 1,1,2-Trichloroethane was detected (but not quantified) in the drinking water supply in Miami, Florida (EPA 1975c). Neither the National Organics Monitoring Survey, nor the National Organics Reconnaissance Survey for Halogenated Organics (Symons et al. 1975) addressed 1,1,2-trichloroethane in drinking water supplies.

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4.0 ENVIRONMENTAL DISTRIBUTION

4.1 INTRODUCTION

This chapter contains information concerning environmental distribution and environmental fate for the trichloroethanes. The scientific literature and EPA's STORET Water Quality files were searched for information pertaining to ambient environmental levels of the chemicals and concentrations in foods. The environmental fate of the two chemicals was assessed. In both cases. little information was found for 1,1,2-trichloroethane. The 1,1,1- isomer was well characterized with respect to both topics.

Concentrations of the chemicals in natural surface waters are generally below 10 µg/l, although, in a small number of cases, higher concentrations have been detected. For both trichloroethanes, the principal fate pathway is volatilization from surface water followed by slow decomposition in the atmosphere. The 1,1,1- isomer has an atmospheric lifetime of six to ten years, while 1,1,2-trichloroethane apparently decomposes more quickly.

Section 4.2 presents monitoring data. Sections 4.3 and 4.4 discuss aspects of environmental fate.

4.2 MONITORING DATA

Trichloroethanes are found in ambient air and water. These compounds have also been detected in foods and in aquatic biota.

Table 4-1 exhibits concentrations of 1,1,1-trichloroethane reported in published literature for the U.S. The levels reported are generally in the low µg/m^3 range or less. Background levels of this isomer pervasive on a global scale are less than 1 µg/m^3. (Correia *et al.* 1978, Su and Goldberg 1979). Concentrations in foreign countries, in both cities and rural areas, are generally <10 µg/m^3. Average atmospheric concentrations of 1,1,2-trichloroethane found in seven cities were in the 40-250 ng/m^3 range (Singh *et al.* 1979, 1980). No other data were found for the 1,1,2-isomer in air.

Table 4-2 displays concentrations reported in the literature for drinking water (surface and groundwater supplies), ambient surface water and wastewater. Most reported data are for the 1,1,1- isomer Though reported values range up to 16,500 µg/l near a production site, most levels are in the low µg/l range. Indeed, these published values are consistent with trichloroethane concentrations in ambient and effluent waters reported from the STORET data base.

Ambient and effluent concentrations of 1,1,1- and 1,1,2-trichloroethane are usually less than or equal to 10 µg/l. This percentage of STORET observations no greater than 10 µg/l resulting from sampling in ambient waters is 86 for 1,1,1-trichloroethane and 90 for 1,1,2-trichloroethane; in effluent waters, the percentage is 90 for 1,1,1-trichloroethane and 96 for 1,1,2-trichloroethane.

TABLE 4-1a. CONCENTRATIONS OF 1,1,1-TRICHLOROETHANE DETECTED IN THE ATMOSPHERE

Sample Date	Location	Concentration	Comment	Reference
BACKGROUND		Max. Min. Mean		
9/16 - 19/74	White Face Mountains, NY	0.71 0.17 0.37 μg/m^3	Concentration varies with urban plume passage.	Lillian et al. (1975)
11/24 - 30/75	Lower end, San Francisco Bay	Avg. 423 ng/m^3 σ 34 ng/m^3	75 samples 100% detection	Singh et al.(1977)
12/02 - 12/75	Point Reyes, CA	Avg. 492 ng/m^3 σ 58 ng/m^3	Avg. 458 ng/m^3 300 samples 100% detection	
March,1976	Pullman, WA (rural)	Mean 515 ng/m^3 σ 47 ng/m^3 26 samples	CH_3CCl_3 0-14.6 km altitude Concentration decreases with intrusion into stratosphere	Cronn et al. (1977)
March 10,1976	Western Montana	530 ng/m^3	At tropopause height, 11.4 km MSL Troposphere average	Cronn & Harsch (1979)
May,1976	Badger Pass, CA	Mean 533 ng/m^3 Std. Dev. 52 ng/m^3	12% increase over May 76 - May 77	Singh et al. 1978
November,1976	St. Francis National Forest Helena, AR	$\leq$1.7 μg/m^3	Background Site	Battelle (1977)
May,1977	Point Arena, CA	Mean 598 ng/m^3 Std. Dev. 97.7 ng/m^3	12% increase over May 76 - May 77	Singh et al. (1978)
URBAN AREAS		Max. Min. Mean		
6/27 - 28/74	New York City, 45th & Lexington	8.7 0.55 3.3 μg/m^3		Lillian et al. (1975)
8/78 - 12/73	Bayonne, NJ	78.5 0.41 8.7 μg/m^3		
7/08 - 10/74	Delaware City Del. Rte. 448 & Rt. 72 Int.	1.6 0.16 0.55 μg/m^3		"
7/11 - 12/74	Baltimore, MD Fort Holabird Area	1.14 0.24 0.65 μg/m^3		"
May,1976	Riverside, CA Airport, 610 m	5.9 μg/m^3		"
August,1978	Claremont, CA	27 μg/m^3		Cronn (1980)
7/17/74 1228	Wilmington, OH, 5000 ft., above inversion	0.14 μg/m^3		" Lillian et al. (1975)
7/17/74 1203	Wilmington, OH, 1500 ft., inversion layer	0.35 μg/m^3		"

TABLE 4-1a. CONCENTRATIONS OF 1,1,1-TRICHLOROETHANE DETECTED IN THE ATMOSPHERE (Continued)

Sample Date	Location	Concentration		Comment		Reference
4/74 - 10/75	LaJolla, CA	<0.32 - 5.9 $\mu g/m^3$				Su & Goldberg (1976)
1/29/74 0800	Washington, DC	2.7 $\mu g/m^3$		Continental U.S.		
4/6/74 1130	Los Angeles, Chinatown, CA	1.8 $\mu g/m^3$				"
4/6/74 1400	Santa Monica Residential Area, CA	7.0 $\mu g/m^3$				"
4/16/74 0830 1200 1700	Orange County, CA	2.2 $\mu g/m^3$ 1.5 $\mu g/m^3$ 2.5 $\mu g/m^3$				"
4/19/74 0730	Chicago, Downtown Loop, IL	1.1 $\mu g/m^3$				"
3/15/75	Chicago Airport, IL	1.7 $\mu g/m^3$				"
Urban Areas		Average g/m^3	Standard Deviation	Daily Dose μg/day (23 m^3/day)		
5/15-5/25, 1980	Houston, TX	1.9	1.5	42	13	Singh et al. (1980)
5/29-6/9, 1980	St. Louis, MO	1.3	0.7	28	7	
6/15-6/28, 1980	Denver, CO	3.9	3.0	92	31	
7/1-7/13, 1980	Riverside, CA	4.1	1.4	93	18	
5-6/79	Los Angeles, CA	5.6	3.6	133	45	Singh et al. (1979)
5-6/79	Phoenix, AZ	4.5	3.3	116	39	
7/79	Oakland, CA	1.6	0.9	38	11	
MARINE						
October, 1978	Atlantic Ocean, average	0.4 $\mu g/m^3$		Marine Air		Su and Goldberg (1976)
1974	Southern California	1.0 ± 0.3 $\mu g/m^3$		Marine Air		"
May 9, 1974	Osborn Bank Basin, CA	0.76 $\mu g/m^3$		Marine Air, off California Coast		"
May 9, 1974	Santa Cruz Basin, CA	0.76				
May 9, 1974	San Pedro, CA	1.6				
May 8, 1974	Santa Barbara Basin, CA	1.3 $\mu g/m^3$				"
May 24, 1974	San Diego Trough, CA	0.76 g/m^3				"

TABLE 4-1a. CONCENTRATIONS OF 1,1,1-TRICHLOROETHANE DETECTED IN THE ATMOSPHERE (Continued)

Sample Date	Location	Concentration	Comment	Reference
NEAR PRODUCERS				
November, 1976	Dow Plant A; Freeport, TX	<1.7 - 64 μg/m^3	1,1,1-Producer, distance ≤ 3.2 km,f (direction, distance, time)	Battelle (1977)
December, 1976	Vulcan Materials Co.; Geismar, LA	≤1.7 - 860 μg/m^3	1,1,1-Producer, distance <1 km	"
November, 1976	Ethyl Corporation; Baton Rouge, LA	<1.7 - 22 μg/m^3	1,1,1-Producer, distance, <.3km	"
December, 1976	PPG Industries; Lake Charles, LA	≤1.7 - 47 μg/m^3	1,1,1-Product Site, distance <4 km	"
January, 1977	Boeing; Auburn, WA	2.2 - 5.5 μg/m^3	User site, Distance <3 km	"

TABLE 4-1b. CONCENTRATIONS OF 1,1,2-TRICHLOROETHANE DETECTED IN THE ATMOSPHERE

Urban Areas		ng/m^3		Daily Dose μg/day		
		Average	Standard Deviation	Average	Standard Deviation	
May, 1980	Houston, TX	180	130	3.1	1.8	Singh *et al.* 1980
May-June, 1980	St. Louis, MO	80	30	1.9	0.4	"
June, 1980	Denver, CO	150	60	3.4	0.6	"
June, 1980	Riverside, CA	230	120	5.0	2.1	"
May-June, 1980	Los Angeles, CA	50	30	1	0	Singh *et al.* 1979
May-June, 1980	Phoenix, AZ	90	60	1	1	"
July, 1980	Oakland, CA	40	20	1	0	"

TABLE 4-2. CONCENTRATIONS OF TRICHLOROETHANES DETECTED IN WATER

Sample Type/Date	Location	Concentration	Comment	Reference
DRINKING WATER—SURFACE WATER		1,1,1- 1,1,2- Detected in 3/10 1/10 High Concentration 8.5 µg/ℓ <1.0 µg/ℓ	NORS	EPA (1975)
		Raw Finished No. Samples 105 103 % Positive 12.4 21.8 Mean 0.32 µg/ℓ 0.56 µg/ℓ Median 0.2 0.4 Range 0.1 - 1.2 0.1 - 3.3 Detected 9.9% of finished surface water samples. Mean of all samples = 0.12 µg/ℓ Max. 2,250 µg/ℓ	NOMS } of positive samples	Coniglio et al. (1980)
	All over U.S.	1,1,1- 1,1,2- Detected in 15/330 Not Average of Positives 2.2 µg/ℓ Analyzed Range <0 5-650 µg/ℓ	CWSS Data	Brass (1981)
8-78/6/79	Niagara Falls, NY	<0.33, 1.1 µg/	1,1,1- Finished Drinking Water Supplies	Kim and Stone (1979)
6/12/1978	Poughkeepsie, NY	4 samples, all <5 µg/ℓ		
2/76-2/78	Waterford, NY	0.1 µg/ℓ, ND, 6 samples <2 µg/ℓ		
DRINKING WATER—GROUNDWATER		Raw Finished No. Samples 13 23 % Positive 23.1 21.7 Mean 4.8 µg/ℓ 2.13 µg/ℓ Median 1.1 2.1 Range 0.3 - 13.0 1.3 - 3.0 Detected in 22.2% of finished ground water samples. 23% of 1611 wells tested in three states were positive.	NOMS } of positive samples	Coniglio et al. (1980)

TABLE 4-2. CONCENTRATIONS OF TRICHLOROETHANES DETECTED IN WATER (Continued)

Sample Type/Date	Location	Concentration			Comment	Reference
			No. Wells Tested	% Positive		
	Alabama		80	10	1,1,1-Trichloroethane	Coniglio *et al.* (1980
	Connecticut		1200	?		
	Florida		329	15		
	Idaho		9	11		
	Kentucky		22	0		
	Maine		89	18		
	Massachusetts		163	21		
	New Hampshire		6	0		
	New Jersey		411	48		
	New York		372	9		
	North Carolina		44	2		
	Rhode Island		88	?		
	South Carolina		4	0		
	Tennessee		50	26		
	Washington		32	69		
	New Jersey		1,1,1-	1,1,2-		"
		No. Samples	394	399		
		% Positive	10	66		
		<1.0 μg/ℓ	376	203		
		1-10 μg/ℓ	17	141		
		10-1000 μg/ℓ	1	55		
		>100 μg/ℓ	-	1		
4/28/78	Nassau County, L.I., NY		1,1,1-	1,1,2-		"
		No. Tested	372	372		
		No. Positive	33	50		
		% Positive	9	13		
		Maximum	310 μg/ℓ	300 μg/ℓ		
	All Over U.S.		1,1,1-	1,1,2-	CWSS	Brass (1981)
		Detected in	3/106	Not Analyzed For		
		Average of Positives	2.8 μg/ℓ			
		Range	<0.5-7 μg/ℓ			

TABLE 4-2. CONCENTRATIONS OF TRICHLOROETHANES DETECTED IN WATER (Continued)

Sample Type/Date	Location	Concentration		Comment	Reference
AMBIENT SURFACE WATER					
11/76 - 1/77	Near Production Plants	0.05 µg/ℓ - 16,500 µg/ℓ		Sediment ND - 6.1 µg/kg	Battelle (1977)
		No. Samples	Concentration Range (Mean) (µg/ℓ)		
	Chicago	7	0.5 - 8 (3)	Lake Michigan, sewage plant effluent, filtration plant, channels	Battelle (1977)
	Illinois	11	<1-3 (<1)	Illinois River	
	Pennsylvania	12	<1-3 (<1)	Delaware, Schuylkill, Lehigh Rivers	
	New York City Area	14	<1-2 (<1)	Hudson River and Bays	
	Hudson River Area	1	<1		
	Upper & Mid-Mississippi R	3	<1		
	Lower Mississippi River	1	<1		
	Houston Area	3	1-2 (<1)	Galveston Bay and Channels	
	Ohio River Basin	3	<1		
	Great Lakes	6	<1		
	Tennessee River Basin	2	<1 and 4 (<2)		
WASTEWATER					
1977		Detected 2-300 µg/ℓ		6/129 Raw Waste Samples from Textile Plants	Rawlings and Sanfield (1978)
Pre-1977		Not Detected		0/129 Secondary Effluent Samples	
		Maximum 8 µg/ℓ		3/4 Sewage Treatment Plant Effluents	U.S. EPA (1977)
		1 µg/ℓ		2/18 Finished Waters	
		4 µg/ℓ		25/182 Ambient Samples	

As Table 4-3 exhibits, the majority of STORET data values for trichloroethanes have associated remark codes: ambient data -- 1,1,1-trichloroethane (85%), 1,1,2-trichloroethane (94%); effluent data -- 1,1,1-trichloroethane (76%), 1,1,2-trichloroethane (97%). The remark codes include: J -- estimated value; K -- actual value is known to be less than value given; and U -- material analyzed for but not detected.

A detection limit (K remark) of 10 μg/l appears most frequently in association with observations from sampling in ambient waters -- for 1,1,1-trichloroethane, 34% of the time and for 1,1,2-trichloroethane, 36% of the time. Sampling in effluent waters reflects several frequently used detection limits: 0.01, 1.0, 5 and 10 μg/l. These limits combined account for 52% of the values recorded for 1,1,1-trichloroethane and 81% for 1,1,2-trichloroethane. Levels might therefore be less than or equal to the reported value.

The distribution of unremarked STORET observations is presented in Table 4-4. The majority of ambient and effluent values range between 1 μg/l and 10 μg/l, inclusively; the exception is ambient values recorded for 1,1,2-trichloroethane for which 60% are less than 1 μg/l.

As of October 2, 1980, 80 observations of 1,1,1-trichloroethane in sediment and 79 observations of 1,1,2-trichloroethane were recorded in STORET. The observations reflect regional conditions for the South, Southwest, and West, for sampling has occurred in only ten states: Alabama, Arizona, California, Idaho, Louisiana, Nevada, New Mexico, Oregon, Texas, and Washington. Table 4-5 shows the ranges for unremarked and remarked values and the number of observations within each category.

Dickson and Riley (1976) reported concentrations of trichloroethanes (1,1,1 and 1,1,2-isomers were not distinguished) between 16 ng/g and 2 ng/g in aquatic biota in the United Kingdom.

STORET system also contains observations in fish tissue. Sampling has been conducted in the ambient waters of nine states: Alaska, California, Idaho, Kansas, Louisiana, Nevada, Oregon, Texas, and Washington. The concentration ranges of unremarked and remarked data are presented in Table 4-6.

Only one study (McConnell et al. 1975) provides data concerning 1,1,1-trichloroethane in foods. The sampling was done in the United Kingdom. No data are available concerning concentrations of the 1,1,2-isomer in food. Table 4-7 shows the concentrations of 1,1,1-trichloroethane ranging from 1 μg/kg to 10 μg/kg. PVC used in food storage containers was found to contain the 1,1,1-isomer, but none was found to have contaminated cooking oils purchased in these containers (Gilbert et al. 1978). Subsequent to the study, the manufacturer of the bottles disclosed that 1,1,1-trichloroethane was no longer present in food packaging grades of PVC.

TABLE 4-3. STATUS OF STORET DATA FOR CONCENTRATIONS OF 1,1,1- AND 1,1,2-TRICHLOROETHANE IN AMBIENT WATER AND EFFLUENT

Status	Observations		Range in Values (µg/l)
	Number	% in Range	
Ambient Data:			
1,1,1-trichloroethane			
unremarked	54	15	0.3 - 1600.0
remarked K	213	58	0.3K - 50.0K
remarked U	99	27	0.0U - 10.0U
	366	100.0	
1,1,2-trichloroethane			
unremarked	20	6	0.5 - 58.0
remarked K	214	60	0.5K - 50.0K
remarked U	123	34	0.0U - 10.0U
	357	100.0	
Effluent Data:			
1,1,1-trichloroethane			
unremarked	126	24	0.2 - 7100.0
remarked J	2	--	2.0J - 7.0J
remarked K	360	68	0.0K - 20.0K
remarked U	43	8	0.0U - 5.0U
	531	100.0	
1,1,2-trichloroethane			
unremarked	13	3	1.1 - 3000.0
remarked J	2	-	3.0J - 6.0J
remarked K	411	88	0.0K - 20.0K
remarked U	43	9	0.0U - 5.0U
	469	100.0	

Source: U.S. EPA STORET Water Quality System, as of September 24, 1980.
KEY: J - estimated value; K - actual value less than value given; U - analyzed for but not detected.

TABLE 4-4. DISTRIBUTION OF UNREMARKED VALUES IN STORET FOR CONCENTRATIONS OF 1,1,1- AND 1,1,2-TRICHLOROETHANE IN AMBIENT WATER AND EFFLUENTS

	1,1,1-Trichloroethane				1,1,2-Trichloroethane			
	Ambient		Effluent		Ambient		Effluent	
Concentration (µg/1)	No. Obs.	%	No. Obs.	%	No. Obs.	%	No. Obs.	%
<1	13	24	11	9	12	60	0	-
1-10	22	41	76	60	7	35	6	46
11-100	14	26	28	22	1	5	2	15
101-500	3	6	9	7	-	-	4	31
501-1000	1	2	0	-	-	-	0	-
>1000	1	2	2	2	-	-	1	8
	54		126		20		13	

Source: U.S. EPA STORET Water Quality System, as of September 24, 1980.

TABLE 4-5. CONCENTRATIONS OF TRICHLOROETHANES IN SEDIMENT REPORTED IN STORET

Compound/Status of Observation	No. Observations	Concentration Range (μg/kg)
1,1,1-trichloroethane		
unremarked	15	0.1 - 16.6
remarked K	49	5.0K - 15000.0K
remarked U	16	0.0U - 5U
	80	
1,1,2-trichloroethane		
unremarked	7	0.3 - 7.0
remarked K	56	5.0K - 580.0K
remarked U	16	0.0U - 15000.0U
	79	

Source: U.S. EPA STORET Water Quality System, as of September 24, 1980.

TABLE 4-6. STORET DATA CONCERNING LEVELS OF TRICHLOROETHANES IN FISH TISSUE

Compound/Status Observations		Concentrations
	No. Observations	Range (ug/kg)
1,1,1-trichloroethane		
unremarked	19	0.002 - 0.97
remarked K	47	0.005K - 20.0K
remarked U	7	0.0U
	73	
1,1,2-Trichloroethane		
unremarked	--	--
remarked K	64	0.005K - 20.0K
remarked U	7	0.0U
	71	

Source: U.S. EPA STORET Water Quality System.

TABLE 4-7. LEVELS OF 1,1,1-TRICHLORETHANE DETECTED IN FOODS IN THE UK

Food Type	Concentration (μg/kg)
Meats	
English beef, steak	3
English beef, fat	6
Pig's Liver	4
Oils and Fats	
Olive Oil (Spanish)	10
Cod Liver Oil	5
Castor Oil	6
Fruits and Vegetables	
Potatoes (S. Wales)	4
(NW England)	1
Apples	3
Pears	2
Packet Tea	7
Fresh Bread	2

Source: McConnell *et al.* (1975).

4.3 ENVIRONMENTAL FATE

4.3.1 Overview

The trichloroethanes have high volatilization rates relative to many other organic chemicals due to their high vapor pressures, even though their solubilities are high also (Table 4-8). The primary fate pathway for these chemicals is volatilization from surface water or soil, followed by slow photooxidation in the atmosphere. Atmospheric lifetime due to photooxidation for 1,1,1-trichloroethane is on the order of six to ten years, long enough for global mixing and transport to the stratosphere to occur. (Hemispheric and stratospheric mixing occur on a time scale on the order of a half year to a year.) Decomposition in the stratosphere can release Cl atoms, which may cause ozone depletion. Estimated ozone depletion due to the 1,1,1- isomer are about 1.3% of the total ozone or less, depending on assumptions of continuing release rates. Little information on the amospheric fate was found of the 1,1,2- isomer although it may photooxidize more rapidly than the 1,1,1- isomer.

The following three sections summarize aquatic fate processes, soil transport and volatilization, and atmospheric fate processes.

4.3.2 Aquatic Fate Processes

4.3.2.1 Hydrolysis

Dilling et al. (1975) found that 1,1,1-trichloroethane in sealed tubes had a 6.9-month half-life for hydrolysis at 25°C. Decomposition products were acetic and hydrochloric acids, along with a minor amount of vinylidene chloride. In aerated water in a closed system decomposition occurred with a half-life of about 6 months in either dark or in sunlight. This time is similar to the 6.9 months for hydrolysis.

McConnell et al. (1975) reported that the 1,1,1- isomer is subject to dehydrochlorination at a rate dependent upon pH. Chemical half-life in seawater is estimated to be 9 months at pH 8 and 10°C. The decomposition product is vinylidene chloride, with a minor amount of acetic acid arising by hydrolysis. In aqueous systems, metallic iron was found to accelerate decomposition, but degradation products were not known.

Dilling et al. (1975) inferred from their experiments that 1,1,1-trichloroethane is chemically stable in water. This is probably a reasonable assumption for surface waters particularly in contrast to the much more rapid volatilization rate. However, for 1,,1,1-trichloroethane in groundwater, where volatilization is not possible, hydrolysis may be an active fate mechanism. The 6-9 month half-life for hydrolysis indicates that about 90% of 1,1,1-trichloroethane in an aquifer would be decomposed in about 2 years.

TABLE 4-8. PHYSICAL PROPERTIES OF 1,1,1-TRICHLOROETHANE AND 1,1,2-TRICHLOROETHANE

Property	1,1,1-Trichloroethane[a]	1,1,2-Trichloroethane[b]
Synonyms	Alpha-trichloroethane Methyl chloroform	vinyl trichloride
Molecular formula	CH_3CCl_3	$CH_2ClCHCl_2$
Formula weight	133.41	133.41
Boiling point	74.0 C (165.2 F) (760 mm Hg)	113.7°C
Melting point	-32.62 C (-26.7 F)	-35, -36.7 C
Vapor density	4.6 (air = 1)	4.63 (air = 1)
Specific gravity	1.339 at 20 C (water = 1.000 at 4 C)	1.44 at 20°C (Water = 1.00 at 4°C)
Solubility	4400 mg/l water at 25 C soluble in ethyl ether, ethyl alcohol	4500 mg/l water at 20°C
Density of saturated air	1.6 (air = 1)	--
Concentration of saturated air	16.7% by volume at 25 C	136 g/m^3 at 20°C 225 g/m^3 at 30°C
Vapor pressure	62 mm Hg at 10°C 100 mm Hg at 20°C 127 mm Hg at 25°C 150 mm Hg at 30°C 240 mm Hg at 40°C	19 mm Hg at 20°C 32 mm Hg at 30°C 40 mm Hg at 35°C
Conversion factors-Air (25C 760 mm Hg)	1 g/m^3 = 183 ppm 1 ppm = 5.54 mg/m^3(b)	1 mg/m^3 = 0.18 ppm 1 ppm = 5.55 mg/m^3(b)

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[a] NIOSH 1976

[b] Verschueren 1977

4.3.2.2 Sorption onto Sediments

No information has been found concerning the sorption of trichloroethanes, although the organic carbon partition coeffficient (K_{oc}) for the 1,1,1- isomer is reported to be 180 (Karickhoff *et al.* 1979). The K_{oc} for 1,1,2- isomer is estimated by the method of Chiou *et al.* (1979) to be 57. These K_{oc} values indicate that the trichloroethanes will sorb to a high degree onto organic matter in soils or sediments.

4.3.2.3 Volatilization from Water

Dilling (1977) found that 1,1,1-trichloroethane volatilized with a half-life of 15.3 - 28.2 minutes from a stirred (200 rpm) 250-ml beaker holding 200 ml of a 1 μg/l solution, 6.5 cm deep. Under similar conditions Dilling *et al.* (1975) found a half-life of about 20 minutes for the same isomer. 90% volatilized in 60-80 minutes. For 1,1,2-trichloroethane, the half-life was 21 minutes and the time to 90% loss was reported to be 102 minutes.

The Dow Chemical Company (Battelle 1977) has reported the following evaporation rates from a similar experiment:

Medium	$\tau_{1/2}$ minutes
Tap Water at 25°C	22
Tap Water at 1-2°C	33
3% Salt Solution	25
Water with ∿500 mg/kg peat moss	20
Water with ∿500 mg/kg wet bentonite clay	20
Water with 2.2 mph wind	17

These laboratory measured rates are not directly indicative of volatilization rates from natural water bodies. When compared with volatilization rates found in a similar manner for other organic chemicals, the trichloroethanes will apparently volatilize relatively quickly. Thus, the trichloroethanes will probably volatilize rapidly from natural water bodies when compared with the other organic chemicals.

Appendix D details estimations of volatilization rates from natural water bodies. The half-life for 1,1,1-trichloroethane from a 1 m deep stream flowing at 1 m/sec with a 3 m/sec wind speed is about 4 or 5 hours. For a 10 m deep stream, the half-life increases to about 6.7 days. Time to 90% loss is about three half-lives, or 12 hours to 20 days. For the 1 m/sec current speed, the distance to 90% loss is 43 to 1700 km downstream. These estimates may represent upper limits since other conditions, such as high wind speed or turbulence in the water, would increase the volatilization rate. Estimated volatilization rates for 1,1,2-trichloroethane are similar, but about 20% slower.

4.3.2.4 Biodegradation

Tabak et al. (1980) conducted static culture flask tests to determine the susceptability of the trichloroethanes to microbial degradation. Wastewater microbiota and a yeast extract were used to inoculate 5 mg/l and 10 mg/l solutions of the 1,1,1- and 1,1,2-isomers. Figure 4-1 shows that 15-25% of the 1,1,1- isomer and 55-60% of the 1,1,2- isomer remained after 21 days. Though these results may not be totally representative of susceptability to biodegradation in the environment, they are indicative of the potential for these compounds to biodegrade in the environment and in waste treatment processes.

4.3.3 Soil Transport and Volatilization

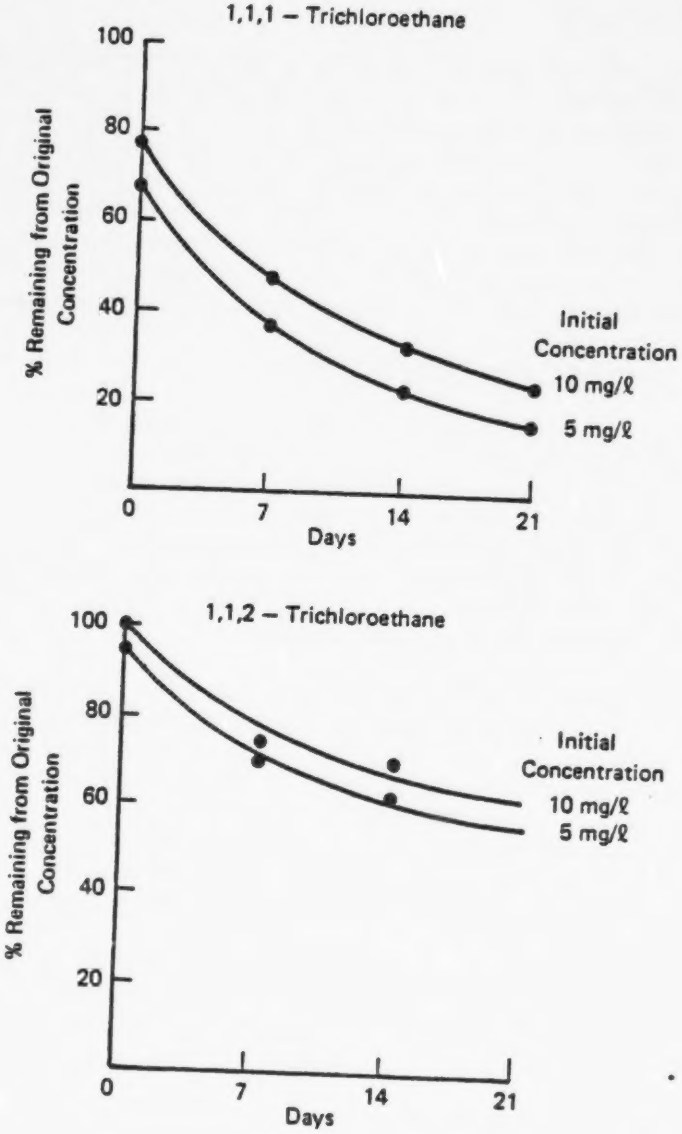
Wilson et al. (1980) studied the transport and fate of chemicals including 1,1,2-trichloroethane applied to a sandy soil composed of 92% sand; 5.9% silt, 2.1% clay and 0.08% organic carbon. The results are somewhat ambiguous since more compound was recovered than was applied. More than half of the 1,1,2-trichloroethane in a water solution apparently volatilized, although more than one-half apparently percolated through the 140-cm soil column (Table 4-9). None was degraded. Soil columns were not saturated.

When Wilson et al. (1980) compared volatilization from the soil column to volatilization from water, they found that volatilization from soil was inhibited by the soil by about a factor of ten or more (for a concentration of 1.00 mg/l applied, the measured flux from soil was 0.36 μg/cm^2/hr vs. a calculated flux of 5.0 μg/m^2/hr from water). For a volatile chemical, such as 1,1,2-trichloroethane, volatilization is probably limited by diffusion through air-filled pores, and not by transport to the surface in soil water or by liquid diffusion.

Transport of 1,1,2-trichloroethane through the soil column, when defined as interstitial water velocity/velocity of pollutant was inhibited minimally by the soil; for sandy soil, the factor was less than 1.5, compared with a predicted value of 1.2.

Several conclusions may be drawn from this study:

- A large part (>50%) of 1,1,2- isomer applied to soil may volatilize.
- A large part (>50%) may percolate through the soil column. The chemical is minimally retarded by sandy soil.
- Volatilization from the soil column will occur at a rate ten or more times slower than from a water column of similar depth.



Note: Samples taken at 7-day intervals.

Source: Tabak et al. (1980)

FIGURE 4-1. FRACTION OF 1,1,1- AND 1,1,2-TRICHLOROETHANE REMAINING DURING BIODEGRADATION TESTS

TABLE 4-9. FATE OF 1,1,2-TRICHLOROETHANE APPLIED TO A SOIL COLUMN IN THE LABORATORY

	Fate (%)		
Concentration Applied, (mg/l)	Volatilized	Column Effluent	Degraded or not Accounted for
1.000	56 ± 16	65 ± 12	-21 ± 10
0.16	95 ± 13	61 ± 5	-56 ± 7

Source: Wilson *et al.* (1980).

In soils in which a large organic matter component is present, volatilization and transport rates will probably be slower than those described here, due to sorption onto the organic matter.

No comparable information has been found for 1,1,2-trichloroethane.

4.3.4 Atmospheric Fate Processes

Appendix E discusses the atmospheric fate of the trichloroethanes in detail. A summary is reported here. Most of the information found related to 1,1,1-trichloroethane with relatively little information found concerning the fate of 1,1,2-trichloroethane in the atmosphere.

The 1,1,1- isomer is long lived in the atmosphere. The residence time based on destruction by photooxidation is estimated to be 6-10 years or longer. Consequently, 12-25% of global emissions will reach the stratosphere to be distributed globally. Actual concentrations vary according to location, latitude, hemisphere, and altitude. Higher concentrations are found in the northern troposphere than in the stratosphere or Southern Hemisphere. Atmospheric concentration, in general, have increased with time due to increasing use of the chemical.

Final disposition of 1,1,1-trichloroethane is in the atmosphere due to photooxidation in both the troposphere and the stratosphere. Chlorine atoms may be released to attack and deplete ozone. Estimates of ozone depletion due to the 1,1,1-isomer are 0.2% to 1.2% of total ozone. In comparison, the total depletion due to chloroflurocarbons released in 1973 is estimated to be about 7% of total steady-state ozone.

The compound 1,1,2-trichloroethane was found to be 30-50 times more reactive than the 1,1,1- isomer when studied in a laboratory photochemical apparatus (see Appendix E). The 1,1,2- isomer photolyzed "rather rapidly" forming formyl chloride, phosgene, and chloroacetyl chloride as decomposition products. The environmental significance of this test was not established; however, the results can be reasonably assumed to indicate that the atmospheric lifetime of 1,1,2-trichloroethane is about a factor of ten less than the lifetime of 1,1,1-trichloroethane, i.e., about 1 year.

4.4 MODELING OF ENVIRONMENTAL DISTRIBUTION

4.4.1 Ambient Concentrations

Fugacity models can be used to estimate ambient environmental concentrations for some chemicals; however, these models are inappropriate for 1,1,1-trichloroethane due to the long lifetime of the chemical, its pervasiveness, and global distribution. Distributions and releases of 1,1,2-trichloroethane appear to be so limited that an equilibrium modeling approach is not appropriate. The model environments and compartments for these chemicals are not clearly defined. The fugacity models were not applied for these reasons.

4.4.2 EXAMS Model Results

For the purpose of estimating the potential fate of 1,1,1- and 1,1,2-trichloroethane in various aquatic environments under conditions of continuous discharge, the EXAMS (Exposure Assessment Modeling System) model AETOX 1 was implemented(U.S. EPA 1980). The physical-chemical properties and reaction rate constants used as inputs are listed in Table 4-9. An arbitrary loading rate of 1.0 kg/hr was chosen for the purpose of comparing the compound's fate in different systems -- a pond, oligotrophic lake, eutrophic lake, average river, turbid river, and coastal plain river. The simulated systems represent "average" U.S. water bodies. Their properties (i.e., biomass, sediment concentrations, climatic conditions) are described in the model output (U.S. EPA 1980) but only flow, length, and depth are given in Table 4-10 for brevity.

Tables 4-11 through 4-15 present the output of the EXAMS simulations by ecosystem type. Presented are average concentrations at equilibrium in various media (water, sediment, biota, etc.) and percentage loss due to different fate processes.

The most significant removal process for the trichloroethanes was volatilization. In the low-flow, physically static systems -- the pond and lakes -- it accounted for more than 90% of the loss, resulting in a system clearance time (assuming cessation of discharge after equilibrium has been attained) of 2 to 4 months for both isomers. Under equilibrium conditions, little of the trichloroethanes mass resided in the sediment, usually less than 11% of the total for both isomers in all systems; the exception was ∿30% of 1,1,1-isomer in sediment in the pond. Chemical oxidation was negligible in all systems. In general, the self-purification time for systems contaminated with 1,1,1-trichloroethane was about 2 times the duration estimated for the 1,1,2- isomer. Persistance was greater in the high biomass systems than in the lower.

In the rapidly flowing river ecosystems, physical transport out of the model's 3-km long reach was obviously more significant than in the other ecosystems. From 62% to 87% of the trichloroethanes mass in a river stretch resided in the sediment. Chemical and biological processes were insignificant. Figure 4-2 plots loss of trichloroethane due to volatilization as a function of distance downstream from the point of release in the river system. Volatilization did not become an important factor for either isomer until approximately 150 km downstream at which point it accounted for approximately 50% of the total. More than 95% of trichloroethane was volatilized at 1500 km downstream.

The average concentration total for both isomers were similar, approximately 3 mg/l in the pond, 0.1 mg/l in the lakes, and approximately 1-10 μg/l in all river systems. Concentrations were a factor of ten higher in the higher biomass coastal plain river. Bottom sediment levels were generally equivalent to water column concentrations; biomass

TABLE 4-10. PARAMETERS FOR TRICHLOROETHANES USED IN EXAMS ANALYSIS[a]

Property	Isomer 1,1,1-	Isomer 1,1,2-	Unit
Molecular Weight	133.4	133.4	g/mole
Solubility	4400	4500	mg/1
Liquid Phase Transport Resistance	0.53	0.53	unitless ratio
Henry's Law Coefficient	3.9×10^{-3}	7.4×10^{-4}	m^3/mole
Vapor Pressure	100	19	torr
Partition Coefficient:			
• Biomass/Water	81	33	$\frac{\mu g/g}{mg/1}$
• Sediment/Water	152	56	$\frac{mg/kg}{mg/1}$
• Octanol/Water	320	117	$\frac{mg/1}{mg/1}$
Chemical Oxidation Rate			
• Water	1	1	mole/1/hr
• Sediment	1	1	mole/1/hr
Hydrolysis Rate	1.7×10^{-4}	1.2×10^{-7}	mole/1/hr

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[a] Source: SRI (1980).

TABLE 4-11. FLOW AND DEPTH OF EXAMS SIMULATED SYSTEMS[a]

System	Water Flow (m^3/day)	Depth (m)		Sediment Mass in Water Column (kg)	Length (m)
		Water Column	Sediment		
Pond	0.643	2	0.05	600	NA
Eutrophic Lake	4.1x5 [b]	20 [c]	0.05	$2695^{(3)}$	NA
Oligotrophic Lake	$4.1\text{x}10^5$ [b]	20 [c]	0.05	$525^{(3)}$	NA
River	$2.4\text{x}10^7$	3	0.05	$6\text{x}10^4$	3
Turbid River	$2.4\text{x}10^7$	3	0.05	$3\text{x}10^5$	3
Coastal Plain River	$2.4\text{x}10^6$	3	0.05	6000	3

---

[a] All data from EXAMS (1980) output.

[b] Average flow for littoral zone, epylimnion and hypolimnion.

[c] Includes epylimnion and hypolimnion (deepest part of lake).

TABLE 4-12. STEADY-STATE CONCENTRATION IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS 1,1,1-TRICHLOROETHANES DISCHARGE AT 1.0 kg/hr[a]

		Maximum Concentrations					
System	Loading	Water Total (mg/1)	Bottom Sediment (mg/1)	Maximum in Sediment Deposits (mg/kg)	Plankton (μg/g)	Benthos (μg/g)	Total Steady-State Accumulation (kg)
Pond	1.0 kg/hr	2.6	2.1	32	210	170	74
Eutrophic Lake		0.13	1.2×10^{-2}	7.1×10^{-2}	10	0.9	310
Oligotrophic Lake		0.14	2.8×10^{-3}	2×10^{-2}	11	0.23	340
River		9.9×10^{-4}	2.5×10^{-4}	2.6×10^{-3}	8×10^{-2}	2×10^{-2}	0.91
Turbid River		9.9×10^{-4}	5.4×10^{-4}	1.9×10^{-3}	8×10^{-2}	4×10^{-2}	0.90
Coastal Plain River		9.3×10^{-3}	2.8×10^{-3}	4.3×10^{-2}	0.75	0.22	8.4

---

[a] All data simulated by EXAMS model (see text for further information).

TABLE 4-13. THE FATE OF 1,1,1-TRICHLOROETHANE IN VARIOUS GENERALIZED AQUATIC SYSTEMS[a]

System	% Residing in Water at Steady-state	% Residing in Sediment at Steady-state	% Transformed by Chemical Processes	% Transformed by Biological Processes	% Volatilized	% Lost by other Proccesses[b]	Time for System Self-Purification[c]
Pond	71	29	1	0	92	7	2700 hours
Eutrophic Lake	99	1	5	0	91	4	56 days
Oligotrophic Lake	>99	<1	6	0	90	4	64 days
River[d]	97	3	0	0	2	98	39 hours
Turbid River[d]	98	2	0	0	2	98	21 hours
Coastal Plain River[d]	93	7	0	0	14	86	180 hours

---

[a] All data simulated by the EXAMS model (see text for further information).

[b] Including loss through physical transport out of system.

[c] Estimate for removal of ca. 75% of the toxicant accumulated in system. Estimated from the results of the half-lives for the toxicant in bottom sediment and water columns, with overall cleansing time weighted according to the toxicant's initial distribution.

[d] All river systems are 3 km in length so that physical transport out of the modeled system is dominant loss process. The "river" system was extended to various lengths up to 100 km from the source to determine the significance of other fate processes (see text).

TABLE 4-14. STEADY-STATE CONCENTRATIONS IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS 1,1,2-TRICHLOROETHANES DISCHARGE AT 1.0 kg/hr[a]

		Maximum Concentrations					
System	Loading	Water Total (mg/1)	Bottom Sediment (mg/1)	Maximum in Sediment Deposits (mg/kg)	Plankton (µg/g)	Benthos (µg/g)	Total Steady-state Accumulation (kg)
Pond	1.0 kg/hr^{-1}	3.4	2.0	12	110	67	76
Eutrophic Lake		0.14	0.007	0.017	4.6	0.2	380
Oligotrophic Lake		0.15	2.1×10^{-3}	5.3×10^{-3}	4.8	0.007	410
River		9.9×10^{-4}	3×10^{-4}	1.2×10^{-3}	3.3×10^{-2}	9.8×10^{-3}	0.9
Turbid River		9.9×10^{-4}	6.2×10^{-4}	9.2×10^{-4}	3.3×10^{-2}	2×10^{-2}	0.9
Coastal Plain River		9.4×10^{-3}	3×10^{-3}	1.8×10^{-2}	0.31	0.1	8.2

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[a] All data simulated by EXAMS model (see text for further information).

TABLE 4-15. THE FATE OF 1,1,2-TRICHLOROETHANE IN VARIOUS GENERALIZED AQUATIC SYSTEMS[a]

System	% Residing in Water at Steady-state	% Residing in Sediment at Steady-state	% Transformed by Chemical Processes	% Transformed by Biological Processes	% Volatilized	% Lost by other Processes[b]	Time for System Self-Purification[c]
Pond	89	11	0	0	91	9	1030 hours
Eutrophic Lake	99	1	0	0	95	5	71 days
Oligotrophic Lake	>99	<1	0	0	94	6	76 days
River[d]	99	1	0	0	1	99	17 hours
Turbid River[d]	99	1	0	0	1	99	12 hours
Coastal Plain River[d]	98	2	0	0	12	88	64 hours

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[a] All data simulated by the EXAMS model (see text for further information).

[b] Including loss through physical transport out of system.

[c] Estimate for removal of ca. 75% of the toxicant accumulated in system. Estimated from the results of the half-lives for the toxicant in bottom sediment and water columns, with overall cleansing time weighted according to the toxicant's initial distribution.

[d] All river systems are 3 km in length so that physical transport out of the modeled system is dominant loss process. The "river" system was extended to various lengths up to 1000 km from the source to determine the significance of other fate processes (see text).

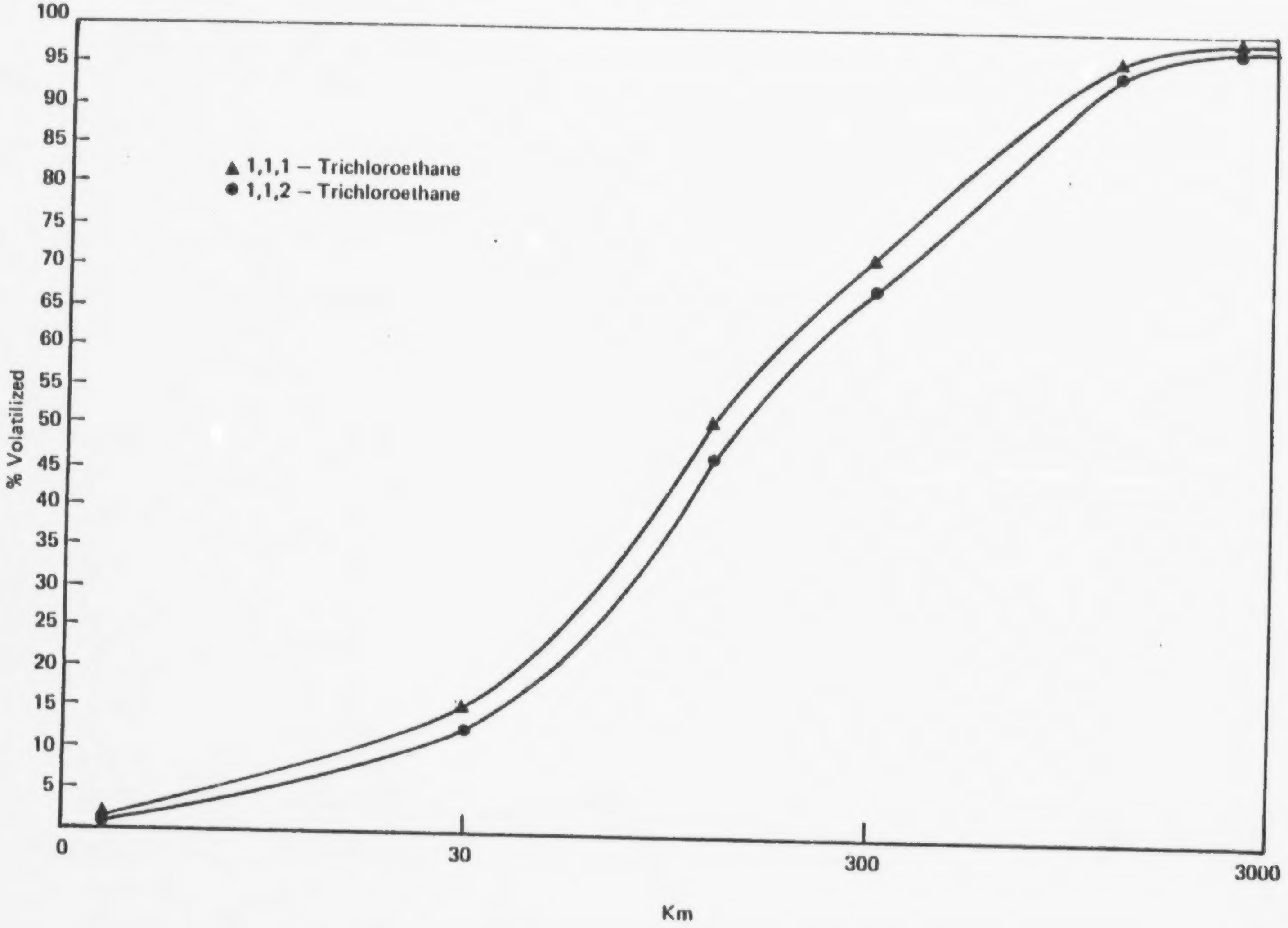

FIGURE 4–2. PERCENTAGE OF TRICHLOROETHANE LOSS DUE TO VOLATILIZATION AS FUNCTION OF DISTANCE FORM POINT SOURCE

concentrations were usually two orders of magnitude greater than water levels. The 1,1,1-isomer had a slightly greater affinity for bioaccumulation and adsorption onto sediment than did the 1,1,2- isomer. This behavior would be expected based on their respective partition coefficients, shown in Table 4-10. The following conclusions can be drawn from the EXAMS analysis about the potential environmental fate of the trichloroethanes in aquatic systems. Persistence depends primarily on volatilization since chemical degradation is minimal. The estimated half-lives (under conditions of continuous discharge) are listed in Table 4-16. The half-lives for the other rivers are not included because the lengths modeled were so short that physical export of the chemical out of the segment was responsible for over 85% of removal. Persistence would be greater in the coastal plain river than in the average river due to the higher biomass retaining some fraction of the chemical. Since volatilization is so important in all systems, conditions of high temperatures, high wind velocity, water and air turbulence, and low biomass would all increase the rate of trichloroethanes to the atmosphere in real systems. This assumes negligible transformation of the compound in both liquid and vapor form. For the 1,1,1- isomer, hydrolysis was detectable as a mechanism of removal in static systems; however, it was never competitive with the process of removal in static systems and it was never competitive with the process of volatilization. In the pond system, a half-life of 5700 hours was estimated for chemical loss alone as compared with a significantly shorter half-life of 60 hours due to volatilization only. As can be seen on Table 4-16, the total system half-life for 1,1,1-trichloroethane was 50 hours, which is quite close to the volatilization half-life.

TABLE 4-16. HALF-LIVES FOR TRICHLOROETHANES PERSISTENCE IN GENERALIZED AQUATIC SYSTEMS

System	Persistence (hrs)	
	1,1,1-	1,1,2-
Oligotrophic Lake	230	280
Eutrophic Lake	210	260
Pond	50	50
River	40	40

Source: U.S. EPA (1980c).

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5.0 EFFECTS AND EXPOSURES--HUMANS

5.1 HUMAN TOXICITY

5.1.1 1,1,1-Trichloroethane

5.1.1.1 Introduction

The principal human exposure route to 1,1,1-trichloroethane, a volatile halogenated hydrocarbon, is by inhalation. It is also readily absorbed from the gastrointestinal tract and via dermal contact. Although anesthetic concentrations of 1,1,1-trichloroethane are capable of depressing the central nervous system, this compound has a fairly low toxicity due to its rapid and almost total elimination as unchanged 1,1,1-trichloroethane.

Commercial samples of 1,1,1-trichloroethane available in the United States contain 3 to 8% by volume of added stabilizers such as p-dioxane, nitromethane, N-methylpyrrole, butylene oxide, 1,3-dioxolane and secondary butyl alcohols (IARC 1979). The following discussion states, whenever possible, whether or not the pure or technical (i.e., stabilized) product was tested.

5.1.1.2 Metabolism and Bioaccumulation

Absorption and Distribution

In both man and rodents, 1,1,1-trichloroethane is rapidly absorbed through the lungs and gastrointestinal tract, and somewhat slower through skin (Stewart 1968, Tsurata 1975).

Studies with humans have demonstrated that between 60-90% of inhaled 1,1,1-trichloroethane is rapidly expired unchanged (Monster 1979, Monster et al. 1979, Humbert and Fernandez 1977). Monster et al. (1979) reported recoveries of 80% and 74%, respectively, following exposure of human volunteers to 382 or 792 mg/m^3 1,1,1-trichloroethane for 4 hours. Total individual uptake was 2.2 times greater with the higher concentration over the 4-hour period. The addition of two 30-minute work periods during the 4-hour exposure increased uptake 2-fold above that noted with exposures at rest, resulting in elimination of 62% of the inhaled dose.

Due to a low blood/gas partition coefficient, retention of 1,1,1-trichloroethane decreases with exposure time, as a steady state is reached. Several studies have noted that pulmonary excretion of 1,1,1-trichloroethane is a function of both exposure duration and concentration. Exposures ranged from a single breath inhalation of the compound to an 8-hour exposure to 1910 mg/m^3. The results of these studies are summarized in Table 5-1.

Absorption of both liquid 1,1,1-trichloroethane and its vapor through human skin has also been demonstrated (Stewart and Dodd 1964, Fukabori et al. 1976, 1977, Riihimaki and Pfaffli 1978). Stewart and Dodd (1964)

TABLE 5-1

PULMONARY ELIMINATION OF 1,1,1-TRICHLOROETHANE IN HUMANS

Exposure	Amount of 1,1,1-Trichloroethane Expired Unchanged	Reference
382 or 1163 mg/m^3 for 8 hr	98% by 8 days	Humbert and Fernandez (1977)
382 or 792 mg/m^3 for 4 hr	70-80% by 8 days	Mónster *et al*. (1979)
775 mg/m^3 for 4 hr with two 30 min. work periods	62% by 8 days	Monster *et al*. (1979)
1910 mg/m^3 for 1 hr	820 mg/m^3 immediately 5.4 mg/m^3 at 24 hr	Stewart *et al*. (1975)
1910 mg/m^3 for 7.5 hr	1365 mg/m^3 immediately 44 mg/m^3 at 16 hr	Stewart *et al* . (1975)
single breath	44% within 1 hr	Morgan *et al*. (1972)

observed rather slow absorption of 1,1,1-trichloroethane during immersion of the hands or thumbs into the solvent or topical application to the hand, all for 30 minutes duration. Average peak breath concentrations were 117, 5.4 and 3.5 mg/m^3, respectively (only 14% of an estimated 820 mg/m^3 exposure), while average breath concentrations 2 hours post-exposure were 8.5, 1.7 and 1.7 mg/m^3 respectively, indicating that amount of absorption is related to skin area and duration of contact. Continuous 30-minute immersion of both hands was estimated to equal a 30-minute exposure to 546-7730 mg/m^3 of this compound. Skin absorption would thus present only a limited health hazard according to these results.

Fukabori and coworkers (1976, 1977) applied liquid 1,1,1-trichloroethane (15 ml) directly to the forearm skin of human volunteers for 2 hours. Unchanged 1,1,1-trichloroethane was quickly detected in expired air reaching 16-38 mg/m^3 by 2 hours. Repetition of this procedure for 5 days produced average alveolar air concentrations of 27 mg/m^3 on day 1 and 60 mg/m^3 on day 4. In another experiment, repeated dipping of both hands into the solvent, 7 times per day for 4 days resulted in blood levels of 6-9 μg 1,1,1-trichloroethane/ml by the fifth day.

Riihimaki and Pfaffli (1978) examined the absorption of 1,1,1-trichloroethane vapors through intact human skin. Two human volunteers with full facepiece respirators were exposed to 3276 mg/m^3 laboratory-grade 1,1,1-trichloroethane in an exposure chamber (15 m^3) for 3.5 hours. Steady and quantitatively increasing blood concentrations of 1,1,1-trichloroethane were noted during percutaneous exposure in contrast to the quick rise and rapid attainment of a steady state in blood subsequent to inhalation exposure. Peak blood concentration at 3.5 hours was ∿90 μg/l; only small amounts of 1,1,1-trichloroethane were exhaled post-exposure. Given the limited number of test subjects, an approximate dermal penetration rate of 0.03 μg/cm^2/hr was calculated. Percutaneous exposure of total body surface to 3276 mg/m^3 for 3.5 hr was estimated to correspond to an equally long inhalation exposure to only 3.3 mg/m^3; i. e., the calculated percutaneous absorption of the vapor was only 0.08% of estimated pulmonary absorption from identical exposures to the same solvent concentration.

Pharmacokinetic studies by various routes of exposure with rats, dogs, mice and monkeys produced similar results to those obtained in humans (Hake et al. 1960, Ikeda and Ohtsuji 1972, MacEwen and Vernot 1974, Holmberg et al. 1977).

Studies concerning the distribution of 1,1,1-trichloroethane include post-mortem data from individuals dying from acute exposure to this compound. Highest tissue concentrations were found in the liver, followed by brain, kidney, muscle, lung and blood (Stahl et al. 1969). Studies with mice exposed to 1,1,1-trichloroethane by inhalation showed solvent concentrations to be of the same general magnitude in kidney, blood and brain at a given exposure concentration, while concentrations in the liver were much higher. Tissue concentrations (especially in the liver) were much greater (nearly 10 times) when animals were exposed to a high air concentration for a short exposure time compared to either a low air concentration for a short exposure time or a low air concentration for a long exposure time even though total exposures (mg/m^3 x hr.) were the same. Exposures ranged from 55 to 54,600 mg/m^3 1,1,1-trichloroethane for durations of 0.5 to 24 hours. The biological half-life of 1,1,1-trichloroethane in the blood, liver, kidney and brain was approximately 20 minutes (Holmberg et al. 1977).

Larsby and coworkers (1978) reported crossing of the blood-brain barrier by 1,1,1-trichloroethane in rabbits. The animals were continuously infused at a rate of 7-19 mg/min intravenously. A near equilibrium between blood and cerebrospinal fluid was achieved very quickly. The rate of elimination after cessation of infusion was rapid during the first 20 minutes, with the concentration of solvent in the cerebrospinal fluid appearing to follow the arterial concentration, but at a lower level.

Biotransformation and Excretion

In controlled human studies, approximately 3.5% of the total uptake is metabolized and excreted in the urine as trichloroethanol or trichloroacetic acid. Monster (1979) suggests that metabolism takes place in the liver by hydroxylation to trichloroethanol followed by subsequent partial oxidation to trichloroacetic acid. The maximum concentration of trichloroethanol in the blood and exhaled air after a 4-hour exposure to 382 or 792 mg/m^3 1,1,1-trichloroethane appeared to occur at about 2 hours post-exposure, and declined rapidly thereafter with a half-life of 10-12 hours. In the post-exposure period, the concentration of trichloroethanol in the blood was approximately 14,000 times greater than that in mixed exhaled air. The maximum concentration of trichloroacetic acid was reached at 20-40 hours after exposure, and decreased exponentially after 60 hours with a half-life of 70-85 hours. Urinary excretion of the major portion of trichloroethanol occurred during the first 24 hours, while only about 30% of the trichloroacetic acid was excreted in the urine by 70 hours. Some 70 hours after exposure, the amount of trichloroethanol and trichloroacetic acid excreted in the urine represented only about 2.0% and 0.5%, respectively, of the uptake of 1,1,1-trichloroethane (Monster 1979, Monster et al. 1979). Humbert and Fernandez (1977) observed that urinary excretion of the metabolites continued for up to 12 days following an 8-hour exposure to similar concentrations (382 or 1162 mg/m^3) of 1,1,1-trichloroethane.

Similar findings were reported by Ikeda and Ohtsuji (1972) for Wistar rats exposed to 1092 mg/kg ^{14}C-labelled 1,1,1-trichloroethane for 8 hours. Urine samples collected for 48 hours from initiation of treatment contained 0.5 mg/kg body weight trichloroacetic acid and 3.1 mg/kg trichloroethanol. Rats intraperitoneally injected with an equimolar dose of 1,1,1-trichloroethane excreted essentially the same levels of both metabolites.

In summary, absorption of 1,1,1-trichloroethane occurs in both humans and animals through inhalation and dermal contact. However, most of the absorbed dose is rapidly eliminated unchanged via the lungs. The small percentage retained and metabolized is converted to trichloroethanol with subsequent conversion to trichloroacetic acid, and excreted in urine. Absorption by the inhalation route appears to be a function of duration as well as concentration. Percutaneous absorption of both liquid and vapor 1,1,1-trichloroethane has been demonstrated in humans but relative to inhalation exposure, dermal contact presents a limited risk.

5.1.1.3 Human and Animal Studies

Carcinogenicity

Three studies have examined the carcinogenicity of 1,1,1-trichloroethane -- by inhalation in rats and by gavage in both rats and mice (Rampy *et al*. 1977, Quast *et al*. 1979, NCI 1977). Poor survival or inadequate duration of study, however, render the data from these studies inadequate for the assessment of human carcinogenic risk.

Technical grade 1,1,1-trichloroethane (95%) stabilized with 3% p-dioxane and containing 2% impurities, was administered in corn oil by gavage to Osborne-Mendel rats (50 per sex per group) at dosages of 750 or 1500 mg/kg, 5 days/wk for 78 weeks and to B6C3F1 mice (50 per sex per group) at time-weighted doses of 2807 or 5615 mg/kg, 5 days/wk for 78 weeks. Rats were observed through 110 weeks, mice through 90 weeks. A slight decrease in average body weight gain was noted for all treated animals of each species. Although no statistically significant increase in either the total number of neoplasms or any specific type of neoplasm was observed in either group of treated rats or mice, an abnormally high early mortality, most probably from chronic murine pneumonia, was such that the number of survivors (3% treated rats, 31% treated mice were alive at termination) render suspect any assessment of carcinogenic risk (NCI 1977).

Rampy *et al*. (1977) and Quast *et al*. (1979) reported no appreciable increase in tumor incidence in Sprague-Dawley rats (90-96 per sex per group) exposed by inhalation to 4.7 or 9.5 g/m^3 1,1,1-trichloroethane 6 hours/day, 5 days/wk for 12 months, followed by an additional 18 months of observation. No differences in body weight, terminal organ weight or mortality were observed. The only reported sign of toxicity was an increased incidence of focal hepatocellular alterations in female rats at the higher dose. No appreciable difference in tumor incidence between treated and control rats was evident. However, the length of treatment was less than lifetime (12 months) and there is a question as to whether or not the maximum tolerated dose was used. These studies, therefore, do not provide adequate data on which to base assessment of carcinogenic risk.

Mutagenicity

The 1,1,1- isomer was weakly mutagenic in *Salmonella typhimurium* strain TA-100 in an Ames test, with or without microsomal activation (Simmon *et al*. 1977).

Price *et al*. (1978) reported *in vitro* transformation of F1706 Fischer rat embryo cells to tumor producing cells following exposure to 1,1,1-trichloroethane. Undifferentiated fibrosarcomas were produced at the site of inoculation in newborn Fischer rats injected subcutaneously with transformed cells.

Adverse Reproductive Effects

No embryotoxic or teratogenic effects were noted in offspring of Sprague-Dawley rats or Swiss Webster mice exposed by inhalation to 4.7 g/m^3 1,1,1-trichloroethane, 7 hours/day on days 6-15 of gestation. The average number of implantation sites per litter, litter size, incidence of fetal resorptions, fetal sex ratio, fetal body measurements, and the incidence of skeletal and visceral anomalies were comparable to control values (Schwetz *et al*. 1975).

Elovarra and coworkers (1979) noted embryotoxic effects in chick embryos subsequent to direct injection of 0.6 to 13.3 μg 1,1,1-trichloroethane/egg on day 3 or 6 of incubation. Weight and growth measurements were affected, but only at the highest dose which was within the upper bound of an approximate LD_{50} of 6.7-13.3 μg/egg. Malformations were increased fourfold above control values but the lack of anatomic and physiologic maternal-fetal relationships and the ultrasensitivity of this test system render it unsuitable for assessing potential teratogenic risks in humans, particularly in view of negative results in two species that possess placentae.

Other Toxicological Effects

Several comprehensive reviews are available on the acute and chronic toxic effects associated with 1,1,1-trichloroethane exposure (Aviado *et al*. 1976, NIOSH 1976a, Walter *et al*. 1976, Kover 1975, MRI 1979). We will, therefore, only highlight those areas that reflect on possible risks from chronic low level exposures.

The primary effect of human exposure to 1,1,1-trichloroethane is depression of the central nervous system. Exposure to 1910 mg/m^3 1,1,1-trichloroethane for 1 hour impaired reaction time and manual dexterity (Gamberale and Hultengren 1978). Another study noted disequilibrium in humans following 20-75 minute exposures to 4900-5460 mg/m^3 (Torkelson *et al*. 1958, Stewart *et al*. 1961). No residual CNS effects, however, have been reported with 1,1,1-trichloroethane exposure.

Liver and kidney damage have been reported in man but only with very high exposures to 1,1,1-trichloroethane. Unlike the CNS effects, however, these changes are irreversible, consisting of actual cellular or biochemical damage including increases in weight accompanied by fatty changes and hemorrhagic necrosis (NIOSH 1976). Dornette and Jones (1960) found no liver damage (measured as serum transaminase) in subjects anesthetized with 32,760-141,960 mg/m^3 1,1,1-trichloroethane for up to 2 hours, while Aviado et al. (1976) report clinically detectable effects on the liver with inhalation of approximately 142,000 mg/m^3 for 15 minutes. Exposures of 2730 mg/m^3 for 78 minutes caused some signs of adverse kidney effects, 4900 mg/m^3 for 20 minutes produced elevated urinary urobilinogen and increasing levels from 0-14,500 mg/m^3 over 15 minutes produced red blood cells in the urine and/or a positive urinary urobilinogen (Stewart et al. 1961).

Inhalation of 54 to 3000 mg/m^3 elicited effects on the cardiovascular system in humans including bradycardia and hypotension within the first few minutes of exposure; in addition to these effects, various alterations in electrocardiogram patterns such as premature ventricular contraction, depressed S-T segments and changes in nodal rhythm were produced with anesthetic levels of 32,760-141,960 mg/m^3 for up to 2 hours (Dornette and Jones 1960).

At least 30 deaths have been attributed to 1,1,1-trichloroethane from deliberate or occupational inhalation exposure, most of which resulted from suffocation with acute edema and congestion of the lungs, liver, brain, kidney and/or spleen (Stahl et al. 1969, Caplan et al. 1976, Bass 1970, Hall and Hine 1966). Tissue concentrations of 1,1,1-trichloroethane were highest in the liver followed by brain, kidney, muscle, lung and blood. Bass (1970) reported 29 cases of sudden death attributed to cardiac sensitization to endogenous catecholamines, while Travers (1974) noted a death from cardiac arrest, all following inhalation of 1,1,1-trichloroethane. Garriott and Petty (1980) reported three fatalities following inhalations of liquid paper solvent containing 0.4-0.7 mg/100 ml 1,1,1-trichloroethane.

A case of accidental ingestion of 600 mg/kg 1,1,1-trichloroethane resulted in initial signs of CNS depression and gastrointestinal effects. Clinical tests showed no adverse effects on CNS, ECG, SGPT, blood urea nitrogen, SGOT, hematocrit and hemoglobin, while some kidney and liver pathology was suggested by red blood cells and protein in the urine and increased serum bilirubin (Stewart and Andrews 1966).

Limited quantitative data are available concerning any toxic effects specifically related to long-term exposure to 1,1,1-trichloroethane by any route of administration. Stewart et al. (1969) reported normal clinical chemistry tests for 11 males after inhalation exposure of 2730 mg/m^3 1,1,1-trichloroethane for 6.5-7 hr/day for 5 days. Subjective reports listed some signs or irritation and slight central nervous effects resulting from exposure.

No clinically pertinent findings (primarily regarding cardiovascular and hepatic effects) were recorded in an epidemiologic study involving two adjacent textile plants, one of which utilized stabilized 1,1,1-trichloroethane as a general cleaning solvent. A total of 151 matched pairs of employees were examined. Employees from the exposed group had occupational exposures to 1,1,1-trichloroethane ranging from 5.5 to 1360 mg/m^3 for up to 6 years (Kramer et al. 1978). A study of health effects associated with air concentrations of 30-1660 mg/m^3 1,1,1-trichloroethane to 170 factory employees also revealed no existing hazard (Hervin and Lucas 1973). Maroni et al. (1977) reported no signs attributed to central or peripheral nervous system impairment in 22 factory workers exposed to air concentrations between 600 and 5400 mg/m^3 for up to 6 years.

Animal studies reflect the same general toxic responses noted in humans. Exposure by various routes of administration to high concentrations of 1,1,1-trichloroethane in various species of animals induces toxic effects on the central nervous system, the cardiovascular and pulmonary systems and in renal and hepatic tissues (Parker et al. 1979, Horiguchi and Horiguchi 1971, Tsapko and Rappoport 1972, Herd et al. 1974, Torkelson et al. 1958, MacEwen and Vernot 1974). In general, the LD_{50}'s for 1,1,1-trichloroethane in most species are in the range of 5,000-12,000 mg/kg bw via oral intake, and 76,450-98,300 mg/m^3 for 3-7 hours via inhalation (MRI 1979).

Torkelson et al. (1958) found slight liver and lung pathology in guinea pigs exposed to 5,460 or 11,000 mg/m^3 1,1,1-trichloroethane for 90 or 30 min/day (respectively) for 3 months. Lung irritation was observed in guinea pigs exposed to 5,460 mg/m^3 for 72 min/day or 11,000 mg/m^3 for 12 min/day, both for 69 exposures. No irritation was evident with exposure to the lower concentration for 36 min/day for 69 exposures.

MacEwen and Vernot (1974) reported no pathology, no hematological effects, normal clinical chemistry tests and no liver lesions in dogs, monkeys, mice and rats with continuous inhalation of 1,365 or 5,460 mg/m^3 1,1,1-trichloroethane for 14 weeks. Lung changes (slight congestion in one half of the rats) was observed at both dose levels, while fatty livers and elevated levels of liver triglycerides in mice were found only at the higher dose. In addition to these effects seen in the mice, McNutt et al. (1975) observed microscopic pathology indicated by centrilobular hepatocyte hypertrophy, focal necrosis and inflammation at week 10 and vacuolization at week 12 with continuous inhalation of 5,460 mg/m^3 for 14 weeks; these effects were not apparent at 1,365 mg/m^3.

In similar studies, Prendergast et al. (1967) found no microscopic pathology, some body weight loss, some leukopenia, normal clinical chemistry tests and some non-specific inflammatory changes in the lungs of monkeys, dogs, rabbits, rats and guinea pigs exposed to 900-2,457 mg/m^3 1,1,1-trichloroethane continuously for 90 days or 14,742 mg/m^3 8 hr/day, 5 days/wk for 6 weeks. Adams et al. (1950) reported similar results for these species with exposures up to 27,300 mg/m^3, 7 hr/day, 5 days/wk for 31-32 exposures.

5.1.2 1,1,2-Trichloroethane

5.1.2.1 Introduction

Although very little data are available concerning toxic, carcinogenic, mutagenic or teratogenic effects in animals or humans, the evidence suggests that 1,1,2-trichloroethane is more toxic that its isomer, 1,1,1-trichloroethane.

5.1.2.2 Metabolism and Bioaccumulation

Available pharmacokinetic data on 1,1,2-trichloroethane indicate that it is readily absorbed from injection sites, skin and via the lungs. Yllner (1971) found that greater than 90% of an intraperitoneal dose of 100-200 mg/kg bw ^{14}C-labelled 1,1,2-trichlorethane in mice was eliminated within 24 hours. Expiration accounted for 16-20% of the administered dose (40% of which was excreted unchanged, 60% as CO_2), and urinary excretion, for 73-87% of the dose. Major urinary metabolites were S-carboxymethyl cysteine (29-46% free, 3-10% bound), chloroacetic acid (6-31%) and thiodiacetic acid (38-42%). Minor metabolites included oxalic acid, glycolic acid, 2,2-dichloroethanol, 2,2,2-trichloroethanol, and trichloroacetic acid, suggesting metabolism via formation of chloracetalydehyde. Only 1-3% remained in the animal after 3 days; 0.1-2.0% was in the feces.

Intraperitoneal injection of guinea pigs with 50 μl of pure 1,1,2-trichloroethane resulted in rapidly increasing blood levels of the solvent, reaching a maximum of nearly 15 μg/ml at 2 hours, then declining over the next 10 hours. Intracutaneous or subcutaneous injection of 50 μl resulted in a slower, more even uptake of the solvent from a depot in or under the skin, and a subsequent slow disappearance from blood (Jakobson _et al_. 1977).

Rapid dermal absorption of 1,1,2-trichloroethane has been documented for guinea pigs (Jakobson _et al_. 1977) and rats (Tsurata 1975, 1977). The compound was detected in the blood of guinea pigs five minutes after application of 1 ml of pure 1,1,2-trichloroethane to the skin. Blood concentrations increased during the first 30 minutes post-dosing, peaking at approximately 3.7 mg/ml. Blood levels dropped to a minimum value (∿2.5 mg/ml) at one hour, but then increased steadily thereafter reaching a concentration of ∿5 mg/ml at 12 hours (length of observation). No indications of blood saturation were noted during this period. A second application at another skin depot, at the point when blood levels were at the minimum from the first exposure, resulted in a distinct short second maximum followed by a second minimum and increase (Jakobson _et al_. 1977). The complex toxicokinetics characteristic of percutaneous application are most likely due to a local effect on and/or within the skin and not to a systemic effect. Jakobson speculates that an increased barrier function of the skin during the first 1-2 hours post-treatment results in a decreased uptake of the solvent into the blood. With time, this barrier is overcome (presumably due to progressive skin damage), leading to a gradual increase in the blood concentration of 1,1,2-trichloroethane.

Another investigator (Tsurata 1975) calculated an in vivo dermal penetration rate for 1,1,2-trichloroethane in rats of 5.6 $mg/min/cm^2$ skin and a percutaneous absorption rate of 17.4 $mg/min/cm^2$ skin. In an in vitro study (Tsurata 1977), with application of 1 ml solvent to excised rat skin (3.7 cm^2 area), 0.53, 1.56 and 3.04 milligrams of solvent had penetrated the skin by 1, 2, and 3 hours, respectively. The penetration curve of 1,1,2-trichloroethane consisted of a lag phase (time period required to establish a steady state diffusion, 0.64 hr) followed by a steady state phase.

The 1,1,2- isomer of trichloroethane is also absorbed via the lungs. Wistar rats exposed by inhalation to 1092 mg/m^3 1,1,2-trichloroethane for 8 hours excreted 0.3 mg/kg bw each of trichloroacetic acid and trichlorethanol in their urine during, and up to 40 hours after exposure (Ikeda and Ohtsuji 1972). An equimolar dose given by intraperitoneal injection (370 mg/kg bw) resulted in similar urinary levels (0.4 mg/kg bw TCA and 0.2 mg/kg bw trichloroethanol) (Ikeda and Ohtsuji 1972).

Van Dyke (1977) reported 9.8% enzymatic dechlorination of 1,1,2-trichloroethane in vitro by rat liver microsomes. Dechlorination was maximal in the presence of O_2 and required NADPH; in a nitrogen atmosphere, dechlorination was reduced to approximately 1/3 - 1/2 the rate under aerobic conditions.

In summation, ready absorption of 1,1,2-trichloroethane from skin, lung and injection site has been demonstrated in laboratory animals. An in vivo dermal absorption rate of 17.4 $mg/min/cm^2$ had been calculated for the rat. Prolonged dermal contact results in a complex pharmacokinetic pattern in guinea pigs which may reflect increased absorption over time resulting from progressive skin damage. Once absorbed, 1,1,2-trichloroethane appears to be rapidly cleared in the urine of rats and mice. Major urinary metabolites identified in mouse urine include S-carboxymethyl cysteine, chloroacetic acid and thiodiacetic acid. Small amounts of trichloroethanol and trichloroacetic acid are also present.

5.1.2.3 Human and Animal Studies

Carcinogenicity

Osborne-Mendel rats (50 per sex per group) were fed technical grade 1,1,2-trichloroethane via stomach tube at time-weighted doses of 46 or 92 mg/kg, 5 days/wk for 78 weeks, followed by observation until week 113. No increased incidence of tumors or appreciable differences in weight gain patterns, appearance or behavior were observed. Survival was such that adequate numbers of rats in all groups were at risk from late-developing tumors (NCI 1978).

In a separate experiment, B6C3F1 mice (50 per sex per group) were fed technical grade 1,1,2-trichloroethane via stomach tube at time-weighted doses of 195 or 390 mg/kg, 5 days/wk for 78 weeks with observation until week 91. A highly significant increased incidence of hepatocellular carcinoma was observed in all mice treated with 1,1,2-trichloroethane (see data below). A positive association between the incidence of pheochromocytoma of the adrenal gland and 1,1,2-trichloroethane exposure was also noted. Adrenal pheochromocytomas were found in 17% (8/48) of high dose males and 28% (12/43) high dose females, but not in low dose groups or controls (NCI 1978).

TABLE 5-2 INCIDENCE OF HEPATOCELLULAR CARCINOMA IN B6C3F1 MICE FED 1,1,2-TRICHLOROETHANE FOR 78 WEEKS

Group	Male	Female
Vehicle Control	2/10 (10%)	0/20 (0%)
Low Dose (195 mg/kg/5 days/wk)	18/49 (37%) p=.022	16/48 (33%) p=.002
High Dose (390 mg/kg/5 days/wk)	37/49 (76%) p<.001	40/45 (89%) p<.001

Source: NCI (1978)

Mutagenicity

A negative mutagenic response was noted with 1,1,2-trichloroethane (8 mg/plate) in a plate assay with *Salmonella typhimurium* strain TA1535 in the presence or absence of a microsomal activation system (Rannug *et al*. 1978). No other data were found concerning possible mutagenic effects of 1,1,2-trichloroethane.

Adverse Reproductive Effects

The embryotoxic effects of 1,1,2-trichloroethane on chick embryos was studied by Elovarra and coworkers (1979). Concentrations of 0.6 to 13.3 µg of 1,1,2-trichloroethane/egg were injected directly in the air sac on day 3 or 6 of incubation. A clear dose-response relationship with respect to survival of the embryos at day 14 was noted regardless of the day of treatment. An approximate LD_{50} value of 6.7-13.3 µg/egg was obtained. Measured weight and growth for live embryos, however, were affected only at the highest dose (13.3 µg/egg). Macroscopic malformations including exteriorization of visera, skeletal and eye abnormalities and profound edema were increased twofold above controls at doses of 0.6 to 13.3 µg/egg. The lack of anatomic and physiologic maternal-fetal relationships and the resultant ultrasensitivity of this system, however, render it unsuitable for assessing potential teratogenic risks to humans.

No additional information was available concerning potential adverse reproductive effects associated with exposure to 1,1,2-trichloroethane.

Other Toxicological Effects

Reports in the literature have linked acute exposure to 1,1,2-trichloroethane with central nervous system effects in mice, kidney necrosis in mice (0.17 ml/kg ip) and dogs (0.4 ml/kg ip) and liver necrosis in both mice and dogs following intraperitoneal injection of high concentrations (Klaasen and Plaa 1966, 1967, Plaa and Larsen 1965, Plaa *et al*. 1958).

Dermal application of 0.5 to 2 ml of 1,1,2-trichloroethane to the skin of guinea pigs resulted in the death of 30 to 75% of the animals within one week (Wahlberg and Boman 1979). In another study, dermal application of 1 ml of the solvent to the skin of guinea pigs produced effects within 15 minutes (pyknotic nuclei in epidermal cells with perinuclear edema in basal cells). After 30 minutes, epidermal separation from the corium and vesicle formation was evident, while within 1-12 hours all layers of epidermis showed cellular degeneration. Damage was localized exclusively to the epidermis (Kronevi *et al*. 1977).

In humans, a narcotic action and irritant effects of eyes and mucous membranes of the respiratory tract are noted following exposure to "low" concentrations of 1,1,2-trichloroethane. It produced cracking and erythema when in contact with the skin. Long-term exposure to the vapor is reported to produce chronic gastric symptoms, fat deposition in the kidneys and damage to the lungs (Hardie 1964). The lowest reported oral lethal dose in man is 50 mg/kg (RTECS 1980).

No case reports or epidemiological studies were available with regard to human exposure to 1,1,2-trichloroethane.

5.1.3 Overview

5.1.3.1 Ambient Water Quality Criteria -- Human Health

The U.S. EPA (1980a) has established a water quality criterion for 1,1,1-trichloroethane of 18.4 mg/l for the maximum protection of human health. The criterion is based on reduced survival noted in Osborne-Mendel rats administered 750 mg/kg of this compound by gavage, 5 days per week for 78 weeks (i.e. 536 mg/kg/day) (NCI 1977). Assuming a 70 kg body weight and a safety factor of 1000, an acceptable daily intake (ADI) of 37.5 mg/day was calculated. The criterion level of 1,1,1-trichloroethane for drinking water, corresponding to this ADI, is 18.4 mg/l.

For the maximum protection of human health from potential carcinogenic effects of exposure to 1,1,2-trichloroethane through ingestion of water and contaminated aquatic organisms, the U.S. EPA (1980a) has set the ambient water concentration at zero. The concentration of 1,1,2-trichloroethane calculated to keep lifetime cancer risk below 10^{-5} is 6 μg/l. The criterion is based on the induction of hepatocellular carcinoma in male B6C3F1 mice given time-weighted average oral doses of 195 or 390 mg/kg, 5 days per week for 78 weeks (i.e., 139 and 279 mg/kg/day, respectively) (NCI 1978).

5.1.3.2 Other Human Effects Considerations

The widely used industrial solvent 1,1,1-trichloroethane has a fairly low toxicity due to rapid and almost total elimination of the compound, unchanged, via the lungs. Pulmonary elimination appears to be a function of both concentration and exposure duration, with retention increasing with concentration but decreasing with increased exposure time. The small amount that is metabolized (∿3.5% of an inhaled dose) is converted by the liver to trichloroethanol and trichloroacetic acid and excreted in urine. Urinary clearance has an approximate half-life in man of 10-12 hours for trichloroethanol and 70-85 hours for trichloroacetic acid. Although inhalation exposure is most common, percutaneous absorption of both liquid and vapor 1,1,1-trichloroethane, as well as exposure via ingestion, has been demonstrated in humans.

In laboratory animals, acute LD_{50}'s range from 5,000-12,000 mg/kg via oral administration and 75,450-98,300 mg/m^3 for 3-7 hours via inhalation exposure. Principal effects of acute exposure in laboratory animals are depression of the central nervous system and disturbances in pulmonary and cardiac function, including sensitization of the heart to epinephrine. In subchronic inhalation studies, monkeys, dogs, rabbits, rats and guinea pigs exposed to 14,750 mg/m^3 8 hours per day, 5 days per week for 6 weeks showed some leukopenia, body weight reduction and non-specific inflammatory changes. The liver appeared to be most susceptible to histopathological changes in guinea pigs and mice.

No adequate carcinogenicity studies are available for the determination of carcinogenic risks associated with exposure to 1,1,1-trichloroethane. In three studies, 1,1,1-trichloroethane caused no significant increase in tumor incidence in B6C3F1 mice (4010 mg/kg/day by gavage), Osborne-Mendel rats (1071 mg/kg/day by gavage) or Sprague-Dawley rats (9555 mg/m^3, 6 hr/day, 5 days per week for 12 months); however, poor survival of test animals and insufficient duration of study rendered these data inadequate for use in an assessment of carcinogenicity. Further data on carcinogenicity and mutagenicity are extremely limited; weakly positive results were reported in one strain (TA100) of *Salmonella typhimurium* and in one mammalian cell transformation assay. No teratogenic effects associated with 1,1,1-trichloroethane exposure were observed in rats or mice exposed to 4780 mg/m^3, 1,1,1-trichloroethane on days 6-15 of gestation.

At low exposures of 1,1,1-trichloroethane ($\leq$ 5460 mg/m^3) the primary effects in man are psychophysiological, including dose-related impairment of perception and coordination and relatively little disturbance in body functions. At anesthetic levels (>43,700 mg/m^3), functional depression of the central nervous system leading to respiratory or cardiac failure are noted. Acute exposures to high levels of the compound (>5460 mg/m^3) by accidental contact or abuse, may result in transient kidney and liver dysfunction. The effects of chronic low-level exposures are not known.

Data concerning the toxicity, carcinogenicity, mutagenicity or teratogenicity of 1,1,2-trichloroethane are very limited or non-existent, particularly regarding adverse effects to man. However, based on the evidence available, 1,1,2-trichloroethane is considered much more toxic than its isomer, 1,1,1-trichloroethane. The greater toxicity of the 1,1,2-isomer may be due to its greater rate of absorption and slower excretion than 1,1,1-trichloroethane.

Absorption of 1,1,2-trichloroethane has been demonstrated in laboratory animals following inhalation exposure or dermal contact. An *in vivo* dermal absorption rate of 17.4 mg/min/cm^2 has been calculated for the rat. Prolonged dermal contact results in a complex pharmacokinetic pattern in guinea pigs which may reflect increased absorption over time due to progressive skin damage. Once absorbed, fairly rapid excretion of 73-87% of an absorbed dose occurs via the urine, and 6-8% of the absorbed dose is expired unchanged. Major urinary metabolites in mice are S-carboxymethyl cysteine, chloroacetic acid, and thiodiacetic acid, and minor amounts of trichloroethanol and trichloroacetic acid.

Exposure to 1,1,2-trichloroethane has been shown to cause central nervous system depression in mice and damage to the liver and kidney in mice and dogs following single intraperitoneal injections of 0.07-0.4 ml/kg. Acute exposure in man appears to be characterized by a narcotic effect on the central nervous system and eye and skin irritation, while possible kidney, lung and gastrointestinal damage may result from long-term exposure.

Data from a study on carcinogenic effects indicated that 1,1,2-trichloroethane caused hepatocellular carcinomas and pheochromocytomas in B6C3F1 mice of both sexes at time-weighted doses of 139 and 279 mg/kg bw/day administered by gavage. Carcinogenicity data from a similar study with Osborne-Mendel rats were inconclusive. No adequate data regarding mutagenic or teratogenic effects associated with 1,1,2-trichloroethane exposure have been reported.

5.1.4 Estimates of Human Dose-Response Relationships

5.1.4.1 1,1,1-Trichloroethane

Poor survival or inadequate exposure duration render the three carcinogenicity studies conducted with 1,1,1-trichloroethane inadequate for the determination of carcinogenic risks. Extremely limited teratogenic and mutagenic data suggest no teratogenic effects in either mice or rats exposed to 4780 mg/m^3 on days 6-15 of gestation and a weakly positive mutagenic response in an in vitro neoplastic transformation assay and a single bacterial strain. The sole lifetime exposure data available for estimation of noncarcinogenic risk are the NCI (1977) findings of reduced survival, most probably from chronic murine pneumonia, in Osborne Mendel rats administered 750 mg 1,1,1-trichloroethane/kg by gavage, 5 days/week for 78 weeks (i.e., 750 mg/kg x 5/7 days = 536 mg/kg/day). An acceptable daily intake (ADI) can be calculated from these data for an average 70 kg human adult. An uncertainty factor of 1000 was included due to the limited chronic toxicity data available for this compound. From these data, an ADI of 37.5 mg/day was obtained.

$$\text{ADI} = \left(\frac{750\ \text{mg/kg} \cdot 5/7\ \text{days}}{1000}\right)\left(70\ \text{kg}\right) = 37.5\ \text{mg/day}$$

5.1.4.2 1,1,2-Trichloroethane

Introduction

The potential carcinogenic risk to humans due to 1,1,2-trichloroethane exposure is estimated below.

Ideally, this problem would be dealt with in two ways:

1) Various extrapolation models would be applied to occupational vs. ambient* human exposure data (from retrospective studies) in order to obtain an approximate dose/response relationship.

2) These same models would be applied to data from controlled experiments on laboratory animals, and the animal dose/response relationship would be converted to an estimated human dose/response.

In the first approach, the overriding uncertainty is in the data themselves: usually the exposure levels, lengths of exposure, and even response rates (responses per number exposed) are "best estimates," and, furthermore, unknown factors (background effects, etc.) may bias the data. In the second approach, the data are usually more accurate, but the relationship between animal and human response rates must be questioned, and at present there is no universally accepted solution to this problem. (In short, in the former case relevant data are of questionable accuracy, whereas in the latter accurate data are of questionable relevance.) If it is possible to perform both analyses and the results corroborate each other, confidence is gained in these results. If, on the other hand, data are not available for one of the analyses and some result is assumed to be better than no result, the analysis must be performed based upon the available data.

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*(or ambient, location A vs. ambient, location B)

Further complicating the issue is that at present there is no basis for judging the relative merits of the various extrapolation models. It is impossible to say which, if any, of them is correct. However, the models as applied here are believed to be conservative, i.e., tend to overestimate the true risk.

The available data concerning human and other mammalian effects were discussed in Section 5.1.2. For 1,1,2-trichloroethane, the only quantitative carcinogenicity data currently available are from an NCI study on Osborne-Mendel rats and B6C3F1 mice. The data selected for extrapolation are listed in Table 5-2.

Data from a study on carcinogenic effects indicated that 1,1,2-trichloroethane caused hepatocellular carcinoma in B6C3F1 mice of both sexes at time-weighted doses of 139 and 279 mg/kg bw/day administered by gavage. A relatively minor incidence of pheochromocytomas of the adrenal gland in the high-dose males and females has not been included. The test performed on Osborne-Mendel rats, also with 1,1,2-trichloroethane by stomach tube, yielded negative results (U.S. EPA 1980a).

To deal with the uncertainties inherent in extrapolation, three commonly used dose/response models have been applied to the data in Table 5-3 to establish a range of potential human risk. The assessment of potential human risk based on these models is subject to important qualifications:

- Though positive carcinogenic findings exist, there have also been negative findings in tests with other species (see above). In view of possible species differences in susceptability, pharmaco-kinetics, and repair mechanisms, the carcinogenicity of 1,1,2-trichloroethane to humans is far from certain.
- Assuming that the positive findings indeed provide a basis for extrapolation to humans, the estimation of equivalent human doses involves considerable uncertainty. Scaling factors may be based on a number of variables, including relative body weights, body surface areas, and life spans.
- The large difference between the typically high experimental data and the actual human exposure levels introduce uncertainty into the extrapolation from animals to humans. Due to inadequate understanding of the mechanisms of carcinogenesis, there is no scientific basis for selecting among several alternate dose/response models, which yield differing results.

TABLE 5-3. CONVERSION OF CARCINOGENICITY DATA FOR 1,1,2-TRICHLOROETHANE IN THE MOUSE INTO EQUIVALENT HUMAN DOSES

	Animal Dose[a] (mg/kg/day)	Equivalent Human Dose[b] (mg/day)	Response	Percent	Percent Excess Over Averaged Controls
Male Mice	390	1120	37/49	76	65
	195	560	18/49	37	26
	0 (vehicle control)	0	2/20	10	--
	0	0	2/17	12	--
Female Mice	390	1120	40/45	89	84
	195	560	16/48	33	28
	0 (vehicle control)	0	0/20	0	--
	0	0	2/20	10	--

Source: NCI (1977)

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[a] 5 days per week for 78 weeks of a 96-week lifetime.

[b] $$\underset{\text{(mg/day)}}{\text{Human Dose}} = \underset{\text{(mg/kg/day)}}{\text{Animal Dose}} \times \underset{\text{(kg)}}{\text{Animal Weight}} \times \left(\frac{\text{Human Weight}}{\text{Animal Weight}}\right)^{2/3} \times \left(\frac{5\text{ days}}{7\text{ days}}\right) \times \left(\frac{78\text{ wks}}{96\text{ wks}}\right)$$

Calculations of Human Equivalent Doses

Obtaining a quantitative human risk estimated based on animal data requires first determining the human dose equivalent to a given animal dose. The approach used has been recommended by the US EPA (Arthur D. Little, 1980) and normalizes the dose rate according to body surface area. This approach is relatively conservative, in that it results in a lower equivalent human dose than would be obtained from simple multiplication of animal dose rate (mg/kg/day) by human body weight. Whether the surface area or body weight ratio is the more appropriate normalization factor is still open to debate. Neither ratio is ultimately correct, however, since differing metabolisms and other factors are ignored in either case. Since for mice the weight ratio is roughly 14 times as large as the surface area ratio, the choice of a conversion method introduces an uncertainty of a factor of ten at least.

For the referenced carcinogenic tests on mice (NCI 1978), doses were administered 5 days per week for 78 weeks, beginning when the mice were 5 weeks old, and concluding with a 13-week observation period following the exposure period. Altogether, the mice received doses for 78 weeks of a 96-week lifetime. From this information and assumed body weights of 70 kg for humans and 0.025 kg for mice a human equivalent dose rate was estimated using the following equation:

$$\underset{\text{(mg/day)}}{\text{Human Dose}} = \underset{\text{(mg/kg/day)}}{\text{Animal Dose}} \times \underset{\text{(kg)}}{\text{Animal Weight}} \times \left(\frac{\text{Human Weight}}{\text{Animal Weight}}\right)^{2/3} \times \left(\frac{5 \text{ days}}{7 \text{ days}}\right) \times \left(\frac{78 \text{ weeks}}{96 \text{ weeks}}\right)$$

From this, a dose of 1 mg/kg/day for a mouse is calculated to be equivalent to 2.9 mg/day for a human.

Estimation of Response per Unit of Exposure

The dose/response models used to extrapolate human risk were the linear "one-hit" model, the log-probit model, and the multistage model. Also included in the table are probability (risk) estimates based on the findings of the CAG (U.S. EPA 1980a). The multistage is actually a generalization of the one-hit model, in which the hazard rate is taken to be a quadratic rather than linear function of dose. All of these models are well described in the literature and a theoretical discussion may be found in Arthur D. Little (1980). The one-hit and multistage models assume that the probability of a carcinogenic response during a lifetime is described by

$$P \text{ (response at dose } x) = 1 - e^{-h(x)},$$

where h(x) is the "hazard rate" function. The log-probit model assumes that human response varies with dose according to a log-normal distribution Due to differing assumptions, these three dose/response models usually give widely differing results when effects data are extrapolated from relatively high doses to the low doses typical of environmental exposure.

For the linear one-hit model, the equation

$$P(x) = 1 - e^{-Bx},$$

where P(x) is the probability of response to dose x, is solved for the parameter B.

It may be shown that for a test group subjected to dose x:

$$B_x = \frac{1}{x} \log_e \frac{1 - P_c}{1 - P_t(x)},$$

where P_c is the average control group response and $P_t(x)$ is the response of the test group. We assume that B is given by

$$B \cong (B_{x_1} \cdot B_{x_2} \cdot --- \cdot B_{x_n})^{1/n},$$

the geometric mean of the B_{x_i} from experimental data, and determine that

$$B \cong 1 \times 10^{-3} \text{ per mg/day.}$$

For the log-probit extrapolation, the "probit" intercept A results from the following equation

$$P(x) = \phi\ (A + \log_{10}[x])$$

where ϕ is the cumulative normal distribution function, and P(x) is the excess probability of response, $P(x) = P_t(x)-P_c$, that is, the probability of response due only to exposure to the carcinogen.

This equation makes the assumption that the log-probit dose/response curve has unit slope with respect to the log-dose. From tables of the standard normal distribution, A (the geometric mean of individually determined A_i) is found to be approximately equal to -2.8. This value was used to determine the probability of a response at various concentrations according to the above equation.

The multistage model with a quadratic hazard rate function,

$$h(x) = ax^2 + bx + c,$$

was also fit to the data. For estimating the parameters a, b, and c, a maximum likelihood method was used, aided by a computer program that performed a heuristic search for the best fit. It was found that $a \cong 1 \times 10^{-6}$, $b \cong 1 \times 10^{-5}$, and $c \cong 8 \times 10^{-2}$. The probability of response attributable to dose x is then given by

$$P(x) = 1 - e^{-(ax^2 + bx)}.$$

Note that since the value of the parameter a is not significantly less than the value of b, P(x) varies linearly with dose only for doses below roughly 1 mg/day. Further, since P(x) depends heavily on the quadratic term in the high dose region, the excess risk predicted by the multistage model in the low dose (linear) region is significantly below the risk predicted by the linear one-hit model.

No attempt was made to determine statistical confidence bounds for any of the three models. The uncertainties inherent (a) in choosing a dose/response model and (b) in determining a human equivalent dose make suspect any further purely statistical analyses of the data.

Table 5-4 summarizes the probability (risk) estimates obtained from these three models. Also included in the table are probability (risk) estimates based on the findings of the CAG (U.S. EPA 1980a). The CAG determined an upper bound on excess lifetime probability (risk) due to 1,1,2-trichloroethane ingestion of 5.73×10^{-2} per mg/kg/day = 819 x 10^{-6} per mg/day (assuming a human mass of 70 kg). (Table 5-3 shows only one significant digit.) The discrepancies between the CAG probability predictions and those derived here arise from differing assumptions about the data and about human equivalent dose, from mathematical differences in the dose/response models, and from the fact that the CAG uses a 95% upper confidence bound in calculating its predicted probability. Predicted excess lifetime probability per capita is shown in Table 5-4 for doses ranging from 1 μg/day to 100 mg/day.

According to the U.S. EPA's Water Quality Criteria Document for Chlorinated Ethanes (U.S. EPA 1980a), the maximum allowable concentration of 1,1,2-trichloroethane in water to keep lifetime cancer probability below 10^{-5} is 6.0 μg/l, or about 0.01 mg/day, assuming a daily water consumption of 2 l/day for humans. (Note that the 6.0 μg/l figure is based on assumptions about indirect as well as direct exposure, particularly on average ingestion by humans of fish inhabiting waters at this concentration, and on the concentration in fish arising from this concentration in the water.) The four dose/response models predict an upper bound for probability for this concentration and intake between roughly 10^{-7} and 10^{-5}.

The estimates in Table 5-4 represent probable upper bounds on the true probability, since the dose/response models are believed to be conservative, and the estimation of human equivalent dose is believed to be conservative as well. Note, however, that the gap between the estimates is large in the low-dose region, so there is a substantial range of uncertainty concerning the actual carcinogenic effects of 1,1,2-trichloroethane. However, present scientific methods do not permit a more accurate or definitive assessment of human risk.

TABLE 5-4. ESTIMATED LIFETIME EXCESS PROBABILITY OF CANCER IN HUMANS DUE TO 1,1,2-TRICHLOROETHANE ABSORPTION AT VARIOUS DAILY DOSE LEVELS BASED ON FOUR EXTRAPOLATION MODELS[a]

Extrapolation Model	Estimated Lifetime Excess Risk of Cancer at Indicated Exposure Levels[a]					
	Exposure Level (mg/day): 0.001	0.01	0.1	1	10	100
Linear	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}
Log-Probit	$<1 \times 10^{-8}$	1×10^{-6}	7×10^{-5}	3×10^{-3}	4×10^{-2}	2×10^{-1}
Multistage	1×10^{-8}	1×10^{-7}	1×10^{-6}	1×10^{-5}	2×10^{-4}	1×10^{-2}
CAG	8×10^{-7}	8×10^{-6}	8×10^{-5}	8×10^{-4}	8×10^{-3}	8×10^{-2}

[a] A range of probability is given, based on four different dose-response extrapolation models. The lifetime excess probability of cancer represents the increase in probability of cancer over the normal background incidence, assuming that an individual is continuously exposed to 1,1,2-trichloroethane at the indicated daily intake over their lifetime. There is considerable variation in the estimated risk due to uncertainty introduced by the use of laboratory rodent data, by the conversion to equivalent human dosage, and by the application of hypothetical dose-response curves. In view of several conservative assumptions that were utilized (see Section 5.1.4.2), it is likely that these predictions overestimate the actual risk to humans.

5.2 HUMAN EXPOSURE

5.2.1 Introduction

Monitoring data presented previously in Chapter 4 indicate that trichloroethanes are widely detectable in environmental media, including drinking water and foods. The fate analysis also demonstrated that the trichloroethanes may occur in all environmental media -- air, water, soil, and sediment. As discussed earlier in this chapter, absorption of trichloroethanes can occur via all exposure routes -- ingestion, inhalation, and dermal contact. Therefore, the potential absorption of the trichloroethanes by these three routes was considered in the human exposure analysis. Both the human effects considerations and the monitoring data indicate that the assessment of risk for the trichloroethanes should be conducted for each isomer separately. Therefore, exposure routes were considered separately for 1,1,1-trichloroethane and the 1,1,2- isomer.

5.2.2 Exposure through Ingestion

Data presented previously in Table 4-2 indicate that both isomers of trichloroethane have been detected in some surface and ground sources of drinking water. It is difficult, however, to estimate the level of exposure to trichloroethanes via drinking water on the basis of the available data. In most cases, the concentrations reported were below the detection limits for the analytic procedures used. As will be discussed below, the relative contribution from drinking water to the total human exposure to trichloroethanes appears to be quite small in most cases.

5.2.2.1 1,1,1-Trichloroethane

Coniglio and coworkers (1980) summarized the data on 1,1,1-trichloroethane from federally sponsored surveys of finished drinking water from surface and ground sources (see Table 4-2). Their compilations indicated that approximately 22% of all finished water supplies (both surface and ground sources) contained detectable levels of 1,1,1-trichloroethane. The mean concentration in finished surface-water supply samples where it was detected was 0.56 μg/l; positive samples from finished ground water supplies had a mean concentration of 2.1 μg/l, although the data base for groundwater is much less extensive than for surface water. The EPA STORET data presented previously in Table 4-4 indicate that most quantified samples (14% were quantified) from ambient U.S. water supplies were in the 1-10 μg/l interval. From these data (Coniglio *et al*. 1980, U.S. EPA 1980b), one can make a rough approximation that about 20% of the population may be exposed to 1,1,1-trichloroethane in their drinking water at levels greater than 1 μg/l, and in isolated cases subpopulations may be exposed to levels greater than 10 μg/l. It should be noted that this estimate of the size of the exposed population is at best a very rough approximation since there is wide variation in the size of water supplies, and it is not likely that the available monitoring data for trichloroethanes constitute a representative sample, by size, of the total U.S. water supply.

The above estimation would also indicate that the major portion of the U.S. population, i.e., about 80%, might be exposed to 1,1,1-trichloroethane in drinking water at levels below detection limits. Detection limits vary considerably depending upon the survey, but it is inferred from the data of Coniglio and coworkers (1980), the STORET data (U.S. EPA 1980b) and Brass (1981) that the detection limits range between 0.1 µg/l and 1 µg/l for most surveys.

Thus, for purposes of this study, it is estimated that some 20% of the U.S. population may ingest greater than 2 µg/day of 1,1,1-trichloroethane via drinking water, assuming ingestion of 2 liters of drinking water per day (ICRP 1974). The remaining 80% of the population would, therefore, ingest less than 2 µg/day in drinking water. These values are given in Table 5-4.

A single study by McConnell et al. (1975) reported levels of 1,1,1-trichloroethane measured in various foods (see Table 4-7). These data are from Great Britain and may not be representative of levels in food in the U.S. Nevertheless, these data were utilized to estimate the potential exposure to 1,1,1-trichloroethane from food. The quantity of each food or food group normally consumed, as cited by the USDA (1980), was used to estimate daily intake as shown in Table 5-4. The estimated amount of 1,1,1-trichloroethane ingested in food could be perhaps 2.8 µg/day.

5.2.2.2 1,1,2-Trichloroethane

The monitoring data for the trichloroethanes in water distinguish in some cases between the two isomers, but the data showing positive and quantifiable amounts of 1,1,2-trichloroethane are few. Results of available studies indicate that the isomer is not pervasive at concentrations above detection limits (~1.5 µg/l).

Coniglio et al. (1980) reported on findings for ground water supplies in New Jersey, which indicated that median levels for both isomers were less than 1 µg/l; the maximum level of 1,1,2-trichloroethane, however, was over 100 µg/l (actual values not given). Levels of the 1,1,2- isomer in well water from Long Island's Nassau County were as high as 310 µg/l. These maxima are thought to be very atypical of U.S. water supplies because there is limited use of the 1,1,2- isomer, much of it in captive processes. The materials balance for 1,1,2-trichloroethane also indicates that relatively little is released into the environment (see Chapter 3.0).

No data are available concerning levels of 1,1,2,-trichloroethane in food.

5.2.3 Exposure through Inhalation

5.2.3.1 1,1,1-Trichloroethane

Atmospheric monitoring data, provided in detail in Table 4-1a, indicate the ubiquitous presence of 1,1,1-trichloroethane in air. Urban air clearly contains higher concentrations than most rural and remote areas that have been monitored. Concentrations in air near producers and users of 1,1,1-trichloroethane tend to be higher than in urban areas and show wide fluctuations.

In order to estimate inhalation absorption of trichloroethanes, a respiratory retention of 50% was assumed (Riihimaki and Pfaffli 1978, Lapp et al. 1979). The breathing rate was taken to be 22.4 m^3/day (1.2 m^3/hr for 16 hours falling to 0.4 m^3/hr while asleep.) (ICRP 1974). In the following discussion it will become evident that inhalation absorption contributes the majority of the total daily dose of 1,1,1-trichloroethane and thus proximity to major sources of air emissions have been taken as a basis for depicting four comprehensive exposure scenarios as follows:

1) Rural Remote - air concentration data for seven areas of the United States considered to represent "background" (see Table 4-1a) average about 0.5 $\mu g/m^3$. There is little variation, ranging from a mean of 0.37 $\mu g/m^3$ for White Face Mountain, N.Y. to 0.598 $\mu g/m^3$ for Point Arena, CA. The coefficient of variation ($\frac{\sigma}{mean} \times 100$) for all of these remote areas was only about 10%. Thus, the average inhalation absorption in rural/remote areas of the U.S. is estimated to be about 6 µg/day and may range from an average of 4.1 µg/day to 6.7 µg/day depending upon local conditions.

2) Urban - air concentration data presented in Table 4-1a indicated that most urban air concentrations are considerably higher than rural air concentrations. The data for seven cities from the survey by Singh et al. (1979,1980) is the most recent - averaging 3.3 $\mu g/m^3$. This value was taken as a representative mean urban air concentration. The range of mean urban air concentrations of 1,1,1-trichloroethane at or near ground level from various U.S. cities is from 0.55 $\mu g/m^3$ for Delaware City, DE to highs of 27 $\mu g/m^3$ for Claremont, CA. A wide range of potential exposure levels is also suggested by the high coefficient of variation of about 60% for the air concentration data.

   Thus, the typical inhalation absorption of urban dwellers is estimated to be 37 µg/day and may range from 6 µg/day to 300 µg/day depending upon the urban area.

3) Near Producers and Users - air concentrations show extremely wide fluctuations, probably caused by variations in emission rates and local meteorological conditions. A representative mean could not be estimated from the available data. As an approximation of a

level to which this subpopulation could be exposed on a continuous basis, the mean of the high values and mean of the low values were taken, i.e., 1.8-200 μg/m^3, giving an estimated range of potential inhalation absorption of 20-2200 μg/day. Estimates of inhalation absorption given by Lapp et al.(1979) for persons living near user/manufacturing sites generally fall within the range calculated here.

4) Occupational - a fourth scenario is presented for contrast, Occupational exposures to 1,1,1-trichloroethane were analyzed at the OSHA standard and over a range of observed concentrations in the workplace in order to provide a basis for comparison with the environmental exposure scenarios. The standard set by OSHA for the 1,1,1-isomer is 350 ppm (1900 mg/m^3) as a time-wighted-average (TWA) for the 40-hour work week (NIOSH 1976). NIOSH (1976) reports that the air levels in occupational settings range from 5.4 mg/m^3 to 2200 mg/m^3. The estimated absorbed dose via inhalation at the TWA is 9,100 mg per 8-hr. work day.

One of the uses of 1,1,1-trichloroethane is as part of the propellant gas in aerosol cans, especially those for paint products. About 5,670 kkg/yr were estimated as actual atmospheric releases from this application (Chapter 3.0). There are, at present, no data to indicate levels of 1,1,1-trichloroethane in the air in the immediate vicinity during or after the use of such aerosol cans. Without such data, it is not possible to estimate actual exposure levels. These exposures would presumably be short-term and would affect only small non-occupational subpopulations.

The results of the calculations of exposure for each of the four scenarios are summarized in Table 5-5.

5.2.3.2 1,1,2-Trichloroethane

Available monitoring data for 1,1,2-trichloroethane, which are detailed in Table 4-1b, indicate that an average air concentration in an urban environment is about 0.12 μg/m^3. The highest value reported was a mean of 0.23 μg/m^3 in Riverside, CA. and the lowest reported 0.04 μg/m^3 for Oakland, CA. It is unclear how representative these cities are for all U.S. cities since no other data were available. On the basis of these data, the inhalation absorption of 1,1,2-trichloroethane for urban inhabitants is estimated to average 1.3 μg/day and may range from 0.45 μg/day to 2.6 μg/day. These results are presented in Table 5-6.

TABLE 5-5. ESTIMATED DAILY HUMAN EXPOSURE TO 1,1,1,-TRICHLOROETHANE

ROUTE	Observed Concentration Mean	Range	Exposure Rate or Intake	Exposure Typical	Range
INGESTION					
Drinking Water[a]		(μg/ℓ)	(ℓ/day)	(μg/day)	
20% U.S. population	-	>1	2	-	>2
80% U.S. population	-	<1	2	-	<2
Food Stuffs[b]		(μg/kg)	(g/day)		
Meat	-	3-6	207	0.6-1.2	
Oils and Fats	-	5-10	8	0.04-0.08	
Fruits and Vegetables	-	1-4	343	0.3-1.4	
Bread	-	2	62	0.1	
Tea[c]	-	7	28	0.0006	
INHALATION[d]	($\mu g/m^3$)		(m^3/day)	(μg/day)	
Rural/Remote	0.5	0.37-0.60	22.4	6	4.1-6.7
Urban	3.3	0.55-27	22.4	37	6-300
Near User/Producer	-	1.8-200	22.4	-	20-2200
Occupational	(mg/m^3)			(mg/day)	
	1900	5-2200	9.6	9100	24-10600
Percutaneous (Occupational)[e]			hrs./day		
Liquid (both hands)	-	-	0.08-0.2	-	13-460
Vapor	-	5-2200	8	-	0.03-13

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a) Based on selected data from Table 4-2.
b) Based on data from McConnell et al. 1975 (Table 4-7) and food consumption data from USDA (1980)
c) 20 grams tea leaves per 227 g tea was assumed.
d) Based on selected data from Table 4-1a. A respiratory retention of about 50% was assumed (see text).
e) Based on findings of Riihimaki and Pfaffli (1978) and Stewart and Dodd (1964). Calculations discussed in text.

TABLE 5-6. ESTIMATED DAILY HUMAN EXPOSURE TO 1,1,2-TRICHLOROETHANE

Exposure Route	Observed Concentrations Mean	Observed Concentrations Range	Exposure Rate or Intake	Exposure µg/day Typical	Exposure µg/day Range
Ingestion	µg/l				
Drinking Water					
- Surface	-	ND(<1.5)	2 l/day	-	ND(<3)
- Ground	<1.0	<1-300 (a)	2 l/day	<2	<2-600
Foodstuff	No data			No data	
Inhalation	$\mu g/m^3$				
Urban Areas	0.12	0.04-0.23	22.4 m^3/day	1.3	0.45-2.6
Rural Areas	No data			-	-

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[a] Data from New Jersey and Nassau County wells only. These data are not believed to be representative of widespread conditions although no other data were found.

5.2.4 Percutaneous Exposure

5.2.4.1 1,1,1-Trichloroethane

Human experimental data demonstrated that percutaneous absorption of both vapor and liquid 1,1,1-trichloroethane can occur, (see Section 5.1.1.2), although these exposures would occur primarily in occupational settings. The data of Riihimaki and Pfaffli (1978) indicate that absorption of 1,1,1-trichloroethane vapor would be slow, even at high concentrations. These authors found that at a concentration of 3,263 mg/m^3, an absorption rate of 2.1 mg/hr was observed for 1,1,1-trichloroethane vapor across the total body surface (1.8 m^2) of human volunteers. Utilizing the Riihimaki and Pfaffli (1978) data, a permeability factor of 0.0004 m^3/(m^{2}xhr) was calculated for human skin with 1,1,1-trichloroethane vapor. [Absorption rate (mg/hr) = concentration (mg/m^3) x surface area (m^2) x permeability (m^3/m^2 · hr)]. Utilizing this factor, the absorption rate across the unprotected total body surface area at the time-weighted average occupational standard of 1900 mg/m^3 would be approximately 1.4 mg/hr or 11 mg/work day.

Dermal absorption of liquid 1,1,1-trichloroethane can be very rapid because it dissolves the fat out of the skin making the skin very permeable. The experiments of Stewart and Dodd (1964) indicated that immersion of both hands in 1,1,1-trichloroethane for 0.5 hour was approximately equivalent in terms of absorbed dose to inhalation of vapors at concentrations between 546 µg/m^3 and 7730 µg/m^3. Assuming a 50% respiratory retention (Riihimaki and Pfaffli 1978, Lapp et al. 1980) and a respiratory rate of 0.6 m^3/hr (sedentary rate) (ICRP 1974), the initial absorption rate from both hands is estimated to be between 160-2300 mg/hr. If dermal absorption occurs in certain occupations, it is thought to be short duration, sporadic, and to occur to a small subpopulation of workers. Table 5-5 presents an estimate of potential absorption of the 1,1,1- isomer in the occupational setting for comparative purposes.

5.2.4.2 1,1,2-Trichloroethane

Percutaneous absorption of either vapor or liquid 1,1,2-trichloroethane presumably could occur to approximately the same extent as for the 1,1,1- isomer. More limited use of the 1,1,2- isomer and a much lower TWA (10 ppm or 54 mg/m^3) imply that occupational absorption via the dermal route is not likely to occur to a significant degree.

5.2.5 Total Exposure Scenarios

5.2.5.1 1,1,1-Trichloroethane

Table 5-7 estimates total absorption of 1,1,1-trichloroethane for three general population scenarios and for an occupational scenario. For the urban scenario, inhalation is the major route of exposure to 1,1,1-trichloroethane. As indicated in Tables 4-1a and 5-5, the range of concentrations and, therefore, of estimated daily absorbed dose, is from 10 μg/day to 300 μg/day via inhalation alone. Approximately 74% of the U.S. population (150,000,000 based on the 1970 census) is estimated to be exposed at these levels (U.S. Bureau of the Census 1979).

For the rural scenario, inhalation is still the major exposure route, although ingestion is estimated to contribute about one-third of the total estimated exposure of 9 μg/day. This level of exposure is estimated to apply to 26% of the U.S. population or 54 million people.

For the scenario considering persons who live and work near sites where 1,1,1-trichloroethane is manufactured or used, the range of potential total absorption was estimated to be between 20 μg/day and 2200 μg/day. Inhalation was again the predominant exposure route. The size of this subpopulation was not estimated, although it could be quite large given the widely distributed use of 1,1,1-trichloroethane as a degreasing agent.

In contrast, occupational exposure to 1,1,1-trichloroethane is estimated to be at least one thousand times greater than in the urban scenario. Again, inhalation absorption is probably the most significant contributor to total daily dose, although percutaneous absorption may be quite high for that small subpopulation of workers who use 1,1,1-trichloroethane without appropriate protection for their hands. At the OSHA standard of 350 ppm or 1900 mg/m^3, inhalation absorption is estimated to be 9100 mg per day. As discussed in Section 5.1 (see Table 5-1), at least 60%, and as much as 98%, may be rapidly excreted unchanged via expired air.

5.2.5.2 1,1,2-Trichloroethane

Limited data detailed in Tables 4-1b and 4-2 have been summarized in Table 5-6. Exposure of populations through contaminated water cannot be reliably estimated on the basis of the available data. Certain contaminated ground sources, notably in New Jersey and Long Island, suggest that for an unknown subpopulation, exposure through drinking water may be significant.

Consistent with the monitoring data for the 1,1,1- isomer and with considerations of the fate of the trichloroethanes, inhalation is thought to be the major daily exposure route. On the basis of rather

TABLE 5-7 TOTAL EXPOSURE SCENARIOS FOR 1,1,1-TRICHLOROETHANE

	Estimated Daily Absorbed Dose (Range)			
Route	**Urban**	**Rural**	**Near Sites**	**Occupational**
Ingestion				
Water	<2µg	<2µg	<2µg	<2µg
Foodstuff	3µg	3µg	3µg	3µg
Inhalation	37 (6-300)µg	6 (4-7)µg	- (20-2200)µg	- (24-10,600)mg
Percutaneous	-	-	-	0.03-460 mg
Total	42 (11-305)µg	11 (9-12)µg	>25 (25-2205)µg	- (27-11,000)µg

limited air monitoring data for some large cities, the average daily absorbed dose from inhalation is estimated to be 1.3 μg/day, with a range of 0.45-2.6 μg/day. Since the majority of urban inhabitants receive their water from surface sources and the monitoring data available suggest that the 1,1,2- isomer is not detectable in most surface supplies, the total daily dose has been taken to be given by the inhalation dose. This level of exposure may involve 74% of the U.S. population or the 150,000,000 urban inhabitants (U.S. Bureau of the Census 1979).

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6.0 EFFECTS AND EXPOSURE--NON-HUMAN BIOTA

6.1 EFFECTS ON BIOTA

This section provides information concerning the levels of trichloroethanes that cause mortality or disrupt physiological functions and processes in aquatic organisms. Toxicity information for the trichloroethanes is limited and includes data for only four freshwater and three marine species. Only one study on chronic effects was available.

Both 1,1,1-trichloroethane and 1,1,2-trichloroethane are liquids in the ambient temperature range and are soluble enough in water to be of potential concern as water pollutants. No information was available on the environmental factors that may influence toxicity.

6.1.1 Freshwater Species

Acute toxicity levels in freshwater organisms were determined for bluegill (*Lepomis macrochirus*), *Daphnia magna*, fathead minnows, and the alga *Selenastrum capricornutum*. The lowest concentration at which lethal effects occurred was 18.0 mg/l of 1,1,2-trichloroethane in *Daphnia*. Toxicity data for freshwater species are presented in Table 6-1. The highest concentration tested, 669 mg/l, did not affect the algae (*Selenastrum*). A chronic value of 0.4 mg/l 1,1,2-trichloroethane was determined for the fathead minnow in embryo-larval tests (U.S. EPA 1980). No other chronic data were available.

6.1.2 Saltwater Species

The acute toxicity data base for 1,1,1-trichloroethane to saltwater to organisms is limited to the sheepshead minnow, mysid shrimp, the algae *Skeletonema costatum*, and barnacle larvae (Table 6-2). No data on toxicity of 1,1,2-trichloroethane to marine species were available. The effects of salinity, temperature, or other water characteristics are also unknown. The 1,1,1-isomer was not toxic to *Skeletonema* at the highest test concentration.

6.1.3 Phytotoxicity

The toxicity of 1,1,1-trichloroethane to the green freshwater algae *Selenastrum capricornutum* and the saltwater algae *Skeletonema costatum* were tested, using chlorophyll and a cell number as indicators of growth. Both species were relatively tolerant of the compound at the levels tested. No acute effects were observed at the highest concentrations tested, 669 mg/l, for either *S. capricornutum* or *S. costatum* (U.S. EPA 1980). No data are available on the effects of trichloroethanes on vascular plants.

TABLE 6-1. ACUTE TOXICITY OF 1,1,1- AND 1,1,2-TRICHLOROETHANE FOR FRESHWATER SPECIES

Species	Isomer	96-hr LC_{50}(mg/l)	Reference
Fathead minnow	1,1,1-	52.8 (FT)[1] 105.0(S)[2]	Alexander *et al*.(1978)
Pimephales promelas	1,1,2-	81.7	U.S. EPA (1980)
Bluegill	1,1,1-	69.7	U.S. EPA (1978)
Lepomis macrochirus	1,1,2-	40.2	U.S. EPA (1978)
Cladoceran			
Daphnia magna	1,1,2-	43.0	Adema (1978)

TABLE 6-2. ACUTE TOXICITY OF 1,1,1-TRICHLOROETHANE FOR SALTWATER SPECIES

Species	96-hr LC_{50}(mg/l)	Reference
Mysid Shrimp		
Mysidopsis bahia	31.2 mg/l	U.S. EPA (1978)
Sheepshead minnow		
Cyrpinodon variegatus	70 mg/l	U.S. EPA (1978)
Barnacle larva		
Flominius modestus	7.5 mg/l	U.S. EPA (1978)

6.1.4 Biological Fate

The high fat solubility and low chemical reactivity of 1,1,1-trichloroethane tends to cause bioconcentration; however, this tendency is offset by the compound's high vapor pressure (100 mm at 20°C) and resultant volatility. Neither of the trichloroethanes bioaccumulate strongly; a steady-state bioconcentration factor of 9 for 1,1,1-trichloroethane was measured for Bluegill. Based on the octanol: water partition coefficient of 117, a BCF of 22 was estimated for 1,1,2-trichloroethane (U.S. EPA 1978,1980).

In field experiments where 1,1,1-trichloroethane was detected at 0.5 μg/l in water, fish concentrations were found up to 100 times the concentration in water. No evidence indicated accumulation through food chains, however. Algae have been found to accumulate 1,1,1-trichloroethane in the low μg/l range, at bioconcentration factors less than 100 (Lapp *et al*. 1979). Section 4.3.3.4 discusses the results of laboratory biodegradation tests on the trichloroethanes. No natural biodegradation of the trichloroethanes has been demonstrated.

6.1.5 Conclusions

The lowest level at which adverse effects to aquatic organisms have been experimentally determined for the trichloroethanes is 7.5 mg/l for barnacle larvae. The most sensitive fish species tested is the Bluegill (69.7 mg/l for 1,1,1-trichloroethane; 40.2 mg/l for 1,1,2-trichloroethane). All toxicity values for fish and invertebrates were in the range 0.4 mg/l to 100 mg/l. Algae were quite resistant to trichloroethanes. No acute effects in algae were observed in test concentrations up to 670 mg/l.

6.2 EXPOSURE OF BIOTA

Monitoring data of levels of 1,1,1-trichloroethane in nondrinking water are available from several studies. Battelle (1977) monitored sites upstream and downstream from five 1,1,1-trichloroethane manufacturers' discharge points and at the outfall pipes. In general, the results show that the average concentration found in surface waters above the producer sites was below 2 μg/l for 1,1,1-trichloroethane, except for one site with an average of 132 μg/l (50 m upstream of the plant's outfall). Downstream of the plants, concentrations of 1,1,1-trichloroethane were higher than those upstream in all cases, with average concentrations ranging from a low of 0.8 μg/l to a high value of 169 μg/l. Battelle also sampled a user site, at which 1,1,1-trichloroethane is used for metal cleaning operations. The highest concentration found in the area was 118 μg/l, 1.5 km downstream of the plant (Lapp *et al*. 1979).

The University of Illinois has conducted a study to detect 1,1,1-trichloroethane in surface water at different sites in the United States. Of the 204 sites sampled, 95% showed less than 6 μg/l. Approximately 75% of the sites sampled showed $\leq$1 μg/l. The maximum detected concentration was 8 μg/l in Cook County, Ill. (Lapp *et al*. 1979).

The STORET water quality data base was examined for concentrations of the trichloroethanes in ambient waters in 16 major river basins. Approximately 350 observations have been made of each isomer; of these, 89% of 1,1,1-trichloroethane and 94% of 1,1,2-trichloroethane levels were $\leq$ 10 μg/l, as were nearly all the remaining 1,1,1-trichloroethane levels. Thus, it can be concluded, based on reported monitoring data, that aquatic concentrations of both chemicals will be below 200 μg/l.

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7.0 RISK CONSIDERATIONS

7.1 RISKS TO HUMANS

7.1.1 1,1,1-Trichloroethane

The compound 1,1,1-trichloroethane does not appear to present carcinogenic risks based on data avialable at this time. In addition, no positive mammalian mutagenic or teratogenic effects have been demonstrated However, if exposure levels are high enough, acute or chronic toxic effects may be noted. An acceptable daily intake (ADI) of 37.5 mg/day has been estimated from findings of reduced survival in rats (see 5.1.4.1). Estimated exposures for urban and rural exposed populations are considerably lower than the estimated ADI. Only the estimated absorption by the occupationally exposed population is in the range of the ADI.

Exposure Scenario	Estimated Exposure (absorbed dose)	
Urban Exposure	42 μg/day	
Rural Exposure	11 μg/day	ADI: 37.5 mg/day
Near Sites	25-2,200 μg/day	
Occupational	27-11,000 mg/day	

Consequently, urban and rural populations and populations near user and manufacturing sites appear not to be at risk from chronic exposure to 1,1,1-trichloroethane. Urban exposures are more than 500 times lower than the ADI, which has a safety factor of 1000 included. Rural exposures are 4000 times lower than the ADI. Some of the 130,000 occupationally exposed individuals might be subject to adverse toxic effects from 1,1,1-trichloroethane since their estimated exposure levels are similar to the estimated ADI for 1,1,1-trichloroethane.

7.1.2 1,1,2-Trichloroethane

Because of very limited monitoring data and the consequent limited exposure estimates developed in Chapter 5.0, only very tentative risk predictions can be made regarding 1,1,2-trichloroethane. For the urban population, the average daily exposure from inhalation alone was estimated to be 1.3 μg/day. Table 7-1 presents the estimated excess lifetime cancers per million exposed population at this daily dose using four risk extrapolation models. If this daily dose of 1,1,2-trichloroethane can be taken as representative of that experienced by the urban population (estimated to be 150 million), the incidence of excess lifetime cancers in this population is estimated to be between 1.5 and 150 (i.e., 150 x 0.01 and 150 x 1).

A small subpopulation may be exposed to much higher levels via contaminated drinking water from certain groundwater sources. The size of this population has not been estimated. The range of excess lifetime cancers per million persons exposed to a daily lifetime dose of 0.6 mg/day in this manner is estimated from the four extrapolation models to be between 6 and 1,350. This level of exposure is thought to be extremely atypical, even though monitoring data are limited.

There is considerable uncertainty associated with the estimates in Table 7-1, as considerable controversy exists over the most appropriate model for performing such extrapolations. Moreover, additional uncertainty is introduced into the risk estimates by the choice of a particular set of laboratory data, by the conversion techniques used to estimate human equivalent doses, and by possible differences in susceptibility between humans and laboratory species. Due to the use of a number of conservative assumptions in the risk calculations, the results shown in Table 7-1 most likely overestimate the actual risk to humans.

7.2 RISK TO AQUATIC BIOTA

The toxicity data base for 1,1,1- and 1,1,2-trichloroethane is limited to one invertebrate fish and algal species for both fresh and salt water. The lowest level at which adverse effects to aquatic organisms have been detected in the laboratory is 7.5 mg/l for salt water barnacle larvae. The most sensitive fish species tested is the bluegill (69.7 mg/l for 1,1,1-trichloroethane; 40.2 mg/l for 1,1,2-trichloroethane). All toxicity values for fish and invertebrates ranged from 1.0 mg/l to 100 mg/l. Neither of the trichloroethanes bioaccumulated strongly; a bioconcentration factor of 9 was measured for 1,1,1-trichloroethane (bluegill Lepomis macrochirus), and 22 was estimated for 1,1,2-trichloroethane.

The monitoring data indicate that the concentrations found in most major river basin samples and near production and user sites were in the low μg/l range. The highest reported 1,1,1-trichloroethane level, detected near a manufacturing site, was 169 μg/l. Although no known fish kills or other short-term high concentrations of trichloroethanes have been reported, the possible episodic occurrence of levels of trichloroethanes greater than 10 mg/l would be of greater potential concern than those levels reported heretofore in the monitoring data. The water quality criteria for trichloroethanes (5300 μg/l finished

TABLE 7-1. ESTIMATED LIFETIME EXCESS PROBABILITY OF CANCER IN HUMANS DUE TO ABSORPTION OF 1,1,2-TRICHLOROETHANE AT DOSES OF 0.6 mg/DAY AND 1.3 µg/DAY ON THE BASIS OF FOUR EXTRAPOLATION MODELS[a]

	Estimated Lifetime Excess Cancer Incidence (per million exposed population)[a]			
	Risk Extrapolation Model			
Absorbed Dose	Linear	Log-Probit	Multistage	CAG
1.3 µg/day	1	0.02	0.01	1
0.6 mg/day	600	1350	6	480

[a] A range of incidence is given per million population exposed, based on four different dose-response extrapolation models for two absorbed daily doses. The lifetime excess incidence of cancer represents the increase in incidence of cancer over the normal background incidence, assuming that an individual is continuously exposed to 1,1,2-trichloroethane at the indicated absorbed daily dose over his or her lifetime. There is considerable variation in the estimated risk, due to uncertainty introduced by the use of laboratory rodent data, by the conversion to equivalent human dosage, and by the application of hypothetical dose-response curves. In view of several conservative assumptions that were utilized (see Section 5.1.4), it is likely that these predictions overestimate the actual risk to humans.

water, 240 µg/l surface water for 1,1,1-trichloroethane, 310 µg/l for 1,1,2-trichloroethane) are not exceeded in ambient and effluent waters in the United States, based on information reported in this document. Exposure levels and known effects levels do not overlap. No acute or chronic effects are known to occur at less than 400 µg/l. Risk to aquatic organisms is, therefore, determined to be negligible on a widespread chronic basis.

APPENDIX A

NOTE 1: Total VOC emission ratio from distillation vent in vinyl chloride process = 0.19 g/kg of 1,1,1-trichloroethane produced = 0.19 kg/kkg. Given a 90% removal efficiency for aqueous scrubbers where the VOC emissions are comprised solely of 1,1,1-trichloroethane, then 0.17 kg were captured by control devices and sent to water per 1 kkg of 1,1,1-trichloroethane produced. The remaining 0.02 kg per 1 kkg of 1,1,1-trichloroethane produced escaped to the atmosphere.

NOTE 2: Negligible amounts of 1,1,1-trichloroethane are lost from vents LEC and IS in Figure B1, because the hydrochlorination process is known to convert vinyl chloride to dichloroethane at an approximate efficiency of 98% and 1,1,1-trichloroethane production conditions are not present (EPA, 1979a and 1979b).

NOTE 3: Based on a glycol pot control device efficiency of 95%; and 2% of the wastes that escape the control techniques which are applied to distillation vents to be equal to 0.004 kg per 1 kkg of 1,1,1-trichloroethane produced (EPA, 1979b), that which escapes would emit 0.01 kg VOC/1 kkg of 1,1,1-trichloroethane produced. Also, the estimated composition of the distillation vent gases from a model plant producing 1,1,1-trichloroethane is 35% 1,1,1-trichloroethane. Therefore: 0.35 (0.01 kg VOC)/1 kkg 1,1,1-trichloroethane produced = 0.0035 kg/kkg.

NOTE 4: If 5% of the total VOC wastes are emitted to air (derived in note 3), then 95% was captured by glycol pot control devices and sent to landfill. If the air emission ratio = 0.0035 kg 1,1,1-trichloroethane emitted/1 kkg of 1,1,1-trichloroethane produced, then 87.5 kg or 0.0875 kkg were emitted to the atmosphere when 25,000 metric tons of product were made. Therefore, the ratio of kilograms of 1,1,1-trichloroethane captured by control devices per metric ton of product made is approximately 0.067 and the quantity of total wastes captured per 25,000 kkg of product made was 2 kkg.

NOTE 5: Vinyl chloride and hydrogen chloride (and the recycled overhead stream from the light ends column) react at 35-40°C in the presence of ferric chloride. The reactor effluent is neutralized with ammonia. The resulting solid complex (residual hydrogen chloride, ferric chloride, and ammonia) is removed by the spent catalyst filter as a semisolid waste stream. The filtered hydrocarbon stream is distilled and high-boiling chlorinated hydrocarbons (polymers) are removed as a waste stream. Alternatively, spent catalyst and polymeric material may be removed in a single step by distillation although this simplification is at the expense of 1,1,1-trichloroethane yields.* The overhead from this column is further fractionated into two streams: (1) the lighter components primarily vinyl chloride) hydrogen chloride, and (2) 1,1-dichloroethene and 1,1-dichloroethane. The lighter components are recycled to the hydrochlorination reactor and the 1,1-dichloroethane product is removed at the bottom stream.

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*Dehydrochlorination is favored in the presence of Friedel-Crafts catalyst (e.g., ferric chloride) and at elevated temperatures (e.g. distillation temperatures).

1,1-Dichloroethane and chlorine react in the chlorination reactor at temperatures between 350-400°C and pressures of 2-5 atmospheres. To minimize by-product formation, low molar ratios (e.g., 0.35-0.70) of chlorine to 1,1-dichloroethane are used. Table B3 in Appendix B presents typical reactor effluents found in patent examples. Hydrogen chloride and low boiling organic hydrocarbons are taken overhead. This stream is normally used to supply the hydrogen chloride requirements of this process although it may be used in other oxy-chlorination processes. The bottom stream from the hydrogen chloride column is further fractionated; 1,1,1-trichloroethane is removed overhead and, after the addition of a stabilizer, is stored. The bottom stream from the 1,1,1-trichloroethane column, comprised largely of 1,1,2-trichloroethane, is used as a feedstock for production of other chlorinated hydrocarbons (e.g., tetrachloroethane, trichloroethene and vinylidene chloride).

NOTE 6: Chlorine and ethane react in an adiabatic reactor at approximately 400°C and a pressure of 6 atm. with a residence time of approximately 15 seconds. The reactor effluent (containing ethane, ethene, vinyl chloride, ethylchloride, vinylidene chloride, 1,1-dichloroethane 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, a small amount of other chlorinated hydrocarbons, and hydrogen chloride) is quenched and cooled. The bottom stream from the quench column, primarily tetrachloroethane and hexachloroethane, is removed and the overhead product is fractionated in the HCl column into a chlorinated hydrocarbon stream and light products stream -- ethane, ethene, and hydrogen chloride. The bottom stream from the hydrogen chloride column is sent to the heavy-ends column where it is separated into two streams. 1,2-Dichloroethane and 1,1,1-trichloroethane are removed as a bottom stream and are suitable as feedstock for other chlorinated hydrocarbon processes. The overhead product (principally 1,1,1-trichloroethane, vinyl chloride, vinylidene chloride, ethyl chloride, and 1,1-dichloroethane) is fractionated and 1,1,1-trichloroethane removed as a bottom product. The overhead stream from the 1,1,1-trichloroethane column is fed to the 1,1-dichloroethane column, where 1,1-dichloroethane is separated as the bottom stream and recycled to the chlorination reactor.

Vinyl chloride, vinylidene chloride, and ethyl chloride (the overhead stream) produced as a result of the direct chlorination of ethene are fed to the hydrochlorination reactor, where vinyl chloride and vinylidene chloride react with hydrogen chloride to form

1,1-dichloroethane and 1,1,1-trichloroethane, respectively. Hydrochlorination reaction conditions are approximately 65°C and 4 atm. The reactor effluent stream is neutralized with ammonia. The resulting complex (ammonium chloride - ferric chloride - ammonia) is removed by the spent catalyst filter as a semisolid waste. The filtered hydrocarbon stream is fractionated further: the bottom fraction (primarily 1,1,1-trichloroethane) is recycled to the 1,1,1-trichloroethane column, while the overhead stream (primarily ethyl chloride and 1,1-dichloroethane) is recycled to the chlorination reactor.

NOTE 7: In most cases the vent gases from direct chlorination and oxy-chlorination processes are incinerated or catalytically combusted to recover HCl (EPA, 1975a; McPherson, *et al.*, 1979).

NOTE 8: Calculations for quantity of 1,1,1-trichloroethane contained in heavy ends wastes generated by vinyl chloride "balanced process" (see Appendix B, Figure B3, for waste source location), based on 1978 1,2-dichloroethane production figures.

In 1978, approximately 5.1 x 10^6 kkg of 1,2-dichloroethane were produced by the "balanced process", where approximately 29 kg of solid wastes (heavy ends = reactor tars) were generated per 1 kkg of 1,2-dichloroethane produced, (Lunde, 1965).* Of the total solid wastes generated, 96% was heavy ends (Lunde, 1965). Therefore if the following ratio applies:

$$\frac{\text{.029 kkg of total solid waste}}{\text{1 kkg of 1,2-dichloroethane}}, \quad \text{then:} \quad \frac{1.48 \times 10 \ \text{kkg (total wastes)}}{5.1 \times 10 \ \text{1,2-dichloroethane}}$$

similarily applies; and 96% of 1.48 x 10^5 = 1.42 x 10^5 kkg of heavy ends wastes. According to an EPA report (1975a), approximately 0.8% (by weight) of vinyl chloride heavy ends was 1,1,1-trichloroethane. Therefore, 1,136 kkg of 1,1,1-trichloroethane were contained within the heavy ends. The lower end of the range, 20 kkg, which represents the quantity of 1,1,1-trichloroethane in heavy ends was calculated as follows: Based on quantities of vinyl chloride produced by the "balanced process" in 1978 (i.e., 3.15 x 10^6 kkg) and 0.0008 kkg of heavy ends were generated per 1 kkg of vinyl chloride made, then about 2,520 kkg of heavy ends wastes were generated (EPA, 1975b). If 0.8% (by weight) of the heavy ends is 1,1,1-trichloroethane, then approximately 20 kkg of 1,1,1-trichloroethane were contained in the heavy ends wastes (EPA, 1975a).

---

*The figure representing 1978 1,2-dichloroethane production quantity is at variance with data reported by the United States International Trade Commission who exclude production data for intermediate products. The figure cited above is based upon end product production and reported yields.

NOTE 9: Calculation of 1,1,1-trichloroethane contained in vinyl chloride reactor tars (see Figure B3 in Appendix B for waste source location).

Based on 1978 1,2-dichloroethane production figures via the "balanced process" (5.1×10^6 kkg), and 29 kg of solid wastes (heavy ends + reactor tars) were generated per 1 kkg of 1,2-dichloroethane produced (Lunde, 1965), approximately 1.48×10^6 kkg of total solid wastes were made. Knowing about 4% of the total wastes to be tars, then 5,920 kkg of tars were produced.

According to an EPA report (1975a), about 0.4% (by weight) of the reactor tars was 1,1,1-trichloroethane. Therefore, nearly 24 kkg of 1,1,1-trichloroethane were contained within vinyl chloride reactor tars generated by the "balanced process" in 1979.*

NOTE 10: EPA, 1979e data states that the total industry wide discharge of 1,1,1-trichloroethane at the 1,500 adhesive and sealant establishments is 8 kg/day. Based on a 365 day/year operation, 2,920 kg or 3 kkg of 1,1,1-trichloroethane are discharged industry wide. Of the 1,500 facilities, only seven discharge directly to water, two of which approach zero discharge (EPA, 1979e). Discharge of 1,1,1-trichloroethane directly to surface water appears to be negligible.

The remaining solvent, 22,527 kkg is lost to air during pressure-sensitive adhesive coating processes (spraying the solvent-containing mixture onto a surface), and evaporation of 1,1,1-trichloroethane during application of the product (i.e., use of contact cement). Only 1% or 230 kkg is lost to the atmosphere during product formulation (Miron, 1980) since such operations are performed in closed vessels.

NOTE 11: In an EPA survey of 13 pharmaceutical manufacturing facilities, 1,1,1-trichloroethane was detected in nine of the plant's wastewater streams (EPA, 1980). Thus, the total discharge from these representative plants is 1,165 grams/day or 0.4 kkg per year.

Plant No	Influent (ug/l)	Effluent (ug/l)	Flow rate (mgd)	g/day discharged
12036	22	11	1.20	50
12044	NA	22	0.13	11
12064	110	110	0.26	108
12097	11	--	0.10	-0-
12108	NA	1300	0.14	690

---

*Assuming the 1978 and 1979 vinyl chloride "balanced process" generated similar quantities of 1,2-dichloroethane.

Plant No	Influent (µg/l)	Effluent (µg/l)	Flow rate (mgd)	g/day discharged
12119	110	10	0.05	2
12161	3	--	1.00	-0-
12204	27	33	0.20	25
12257	110	110	0.50	208
12311	17	--	0.16	-0-
12420	110	110	0.17	71
12439	261	12	0.01	.45
12447	720,000	--	1.50	-0-

NOTE 12: Based on EPA data (1980c), average POTW influent equalled 66 µg/l; effluent equalled 10 x 4 µg/l. Using a total nationwide POTW flow of 10^{11} l/day and 365 day/yr operation, 2,410 kkg of 1,1,1-Trichloroethane were contained in POTW influent; 380 kkg in effluent. Based on raw sludge concentration of 30.8 µg/l of 1,1,1-trichloroethane, and a total of 6 x 10^6 kkg dry sludge generated per year which is 95% water (by weight), 4 kkg of 1,1,1-trichloroethane were contained in land-destined POTW sludge in 1978.

10^{11} l/day x 66 µg/l x 365 day/year = 2,410 kkg/yr.

10^{11} l/day x 10 x 4 µg/l x 365 day/year = 380 kkg/yr.

.05 x = 6 x 10^6 x = 1.2 x 10^8 kkg 1.2 x 10^{11} l

1.2 x 10^{11} l x 30.8 µg/l = 3.69 kkg

NOTE 13: Estimated production of 1,1,2-trichloroethane is calculated as follows: 122,450 kkg 1,1-dichloroethylene/yr x 1.528 kkg 1,1,2-trichloroethane per kkg 1,1-dichloroethylene = 187,100 kkg 1,1,2-trichloroethane.

NOTE 14: Some 1,1,2-trichloroethane is discharged with the solid waste generated during 1,2-dichloroethane production. Based on 1975 discharge rates: 2 kg of 1,1,2-trichloroethane discharged/kkg 1,2-dichloroethane produced by direct chlorination x 2.08 x 10^6 kkg 1,2-dichloroethane produced = 4,000 kkg of 1,1,2-trichloroethane generated and contained in solid waste.

APPENDIX B

VINYL CHLORIDE MANUFACTURE VIA THE BALANCED PROCESS

In addition to direct chlorination and oxy-chlorination processes, a pyrolysis (dehydrochlorination) process with attendant purification process has been added. Current yields of dehydrochlorination of 1,2-dichloroethane are on the order of 50 to 60% with selectivities to vinyl chloride of 96-99+% (McPherson et al., 1979). Based on the current yield of 1,2-dichloroethane pyrolysis, with equimolar production of hydrogen chloride (and allowing for losses), capacities of oxy-chlorination and direct chlorination processes are approximately equal.

Crude 1,2-dichloroethane from the oxy-chlorination process is washed with dilute caustic to remove hydrogen chloride and chlorinated by-products (notably chloral) and dried. "Crude" 1,2-dichloroethane from direct chlorination may be combined with this stream and purified for pyrolysis; alternatively 1,2-dichloroethane from direct chlorination may be sufficiently pure for pyrolysis without further purification. After dehydrochlorination, the reactor effluent is quenched with 1,2-dichloroethane and separated by fractional distillation in a series of columns. Hydrogen chloride is recycled to the oxy-chlorination reactor while recovered 1,2-dichloroethane is returned to the 1,2-dichloroethane purification system.

TABLE B.1 1,1,1-Trichloroethane Releases to the Environment from Vinyl Chloride Process in 1979 (kkg)

Producer (Location)	Quantity Produced (x 10^3 kkg/yr)[b]		Waste Sources[c]						
			TC	F_1	HEC	PS	H	F^2	W
Dow Chemical Co. (Freeport, TX)	122	Control Devices/ Techniques[g]	aqueous scrubber	none	none	refrigerated vent condensers	refrigerated vent condensers	detection and correction of major leaks	none
Dow Chemical Co. (Plaquemine, LA)	80		aqueous scrubber	none	none	refrigerated vent condensers	refrigerated vent condensers	detection and correction of major leaks	none
PPG Industries (Lake Charles, LA)	95		recycled	none	none	refrigerated vent condensers	refrigerated vent condensers	detection and correction of major leaks	none
Total:	297								

Source: EPA, 1979a and 1979b.

Producer (Location)	Quantity Dispersed (kkg/yr)[d]																					
	TC			F_1[e]			HEC			PS			H			F^2			W			
	Air[f]	Land	Water	Air	Land	Water	Air	Land	Water	Air[f]	Land	Water	Air[f]	Land	Water	Air	Land	Water	Air	Land	Water	Total
Dow Chemical Co. Freeport, TX	2	neg[h]	21	neg[h]	3	neg[h]	neg[h]	neg[h]	neg[h]	13	neg[h]	71	11	neg[h]	61	5	neg[h]	neg[h]	NA[i]	neg[h]	neg[h]	187
Dow Chemical Co. (Plaquemine, LA)	2	neg[h]	14	neg[h]	2	neg[h]	neg[h]	neg[h]	neg[h]	8	neg[h]	46	7	neg[h]	40	3	neg[h]	neg[h]	NA[i]	neg[h]	neg[h]	122
PPG Industries (Lake Charles, LA)	neg[h]	neg[h]	neg[h]	neg[h]	2	neg[h]	neg[h]	neg[h]	neg[h]	10	neg[h]	55	9	neg[h]	48	4	neg[h]	neg[h]	NA[i]	neg[h]	neg[h]	128
Total	4	neg[h]	35	neg[h]	7	neg[h]	neg[h]	neg[h]	neg[h]	31	neg[h]	172	27	neg[h]	149	12	neg[h]	neg[h]	NA[i]	neg[h]	neg[h]	437

Table B.1 (concluded)

a) See text and Note 5 in Appendix A for supplemental information.

b) Assuming production quantities per plant are similar to those production quantities in 1978; and total production quantity equal to difference between total quantity of 1,1,1-trichloroethane produced (321,830 kkg, Harris, 1980) and quantity of 1,1,1-trichloroethane produced by direct chlorination of ethane (25,000 kkg, Phillips, 1980).

c) TC = 1,1,1-trichloroethane column vent; F_1 = filter, HEC = heavy ends column, PS = product storage; H = handling; F_2 = fugitive emissions; and W = wastewaters from steam stripping; vent losses of 1,1,1-trichloroethane from light ends column and intermediate storage (i.e., vents LEC and IS, Figure B.1) are negligible (see Appendix A, note 2) are assumed to be negligible (EPA, 1979); see Figure B1 for location of waste sites.

d) Kilograms of 1,1,1-trichloroethane dispersed to air (and water)/kkg produced from TC vent with aqueous scrubbers is 0.02 (and 0.17), see note 1, Appendix A; from F_1 vent sent to landfill is 0.022, (Elkin, 1969); from HEC vent without controls is <0.001; from PS, H, and F_2 waste sources controlled with refrigerated vent condensers, or through detection and correction of major leaks, are 0.103, 0.00 and 0.039 to air, respectively, and 0.58, 0.5 and 0 to water, respectively; and W discharges (uncontrolled) are <0.001.

e) Assuming all of the spent catalyst complex (NH_4 $FeCl_3$ NH_3), which is composed primarily of 1,1,1-trichloroethane, with minor quantities of 1,1-dichloroethane, is sent to landfills, (Elkin, 1969).

f) Air emission to be comprised solely of 1,1,1-trichloroethane.

g) Control device/technique efficiencies applied to TC, PS, H and F_2 wastes are 90, 85, 85, and 90%, respectively.

h) Negligible; i.e., <1 kkg.

i) Not applicable.

Source: EPA, 1979a/b.

TABLE B.2 Environmental Releases from 1,1,1-Trichloroethane Production via Direct Chlorination of Ethane Process, 1978 (kkg/yr)[a]

Quantity Produced[b]	Environmental Waste Dispersion Site		Waste Sources[c]							
			TC	(F_1 +Q)	RS	PS	H	F_2	W	Total (kkg/yr)[j]
25,000		Control Devices/ Techniques[d]:	Glycol pot	none	refrigerated vent condenser	refrigerated vent condenser	refrigerated vent condenser	detection and correction of major leaks	none	
		Waste Quantity (kkg/yr)[e]:								
	Air		neg[f]	neg[f,h]	1	3	2	4	NA[i]	10
	Land		2[g]	neg[f,h]	neg[f]	neg[f]	neg[f]	neg[f]	neg[f]	2
	Water		neg[f]	neg[f]	6	15	13	neg[f]	neg[f]	34
	Total (kkg/yr)[j]		2	neg	7	18	15	neg	neg	46

Source: EPA, 1979b.

a) This process is carried out by the Vulcan plant at Geismar, LA.

b) Philips, 1980.

c) TC = 1,1,1-trichloroethane columns vent, 1,1-dichloroethane column vent, and product recovery column vents combined; F_1 = catalyst filter; Q = quench column vent; RS = recycle storage vent; PS = product storage vent; H = handling; F_2 = fugitive emissions; W = wastewaters from steam stripping before discharge to wastewater treatment system; see Figure B.2 for waste source sites.

d) Control device/technique efficiencies applied to TC, RS, PS, H and F_2 vents are 95, 85, 85, 85 and 90% respectively and already included in waste emission/discharge/disposal ratios below.

e) Ratio of kilograms of 1,1,1-trichloroethane dispersed to air and (water) per metric ton produced from TC with glycol pot control device is 0.0035 (see Appendix A, note 3) and (0.067); for uncontrolled air emissions from incineration and releases to landfill from F_1 and Q combined (assuming wastes to be solely composed of 1,1,1-trichloroethane) is < 0.001; from RS, PS and H controlled by refrigerated vent condensers are 0.039, 0.103 and 0.090 to air, respectively and 0.221, 0.58 and 0.51 to water, respectively; F_2 air emissions (assuming to be solely composed of 1,1,1-trichloroethane) controlled by detection and correction of major leaks is 0.178; and W discharges (uncontrolled) is 0.001.

f) Negligible, i.e., <1 kkg.

g) See Appendix A, note 4.

h) Assuming wastes composed solely of 1,1,1-trichloroethane, and 50% of the combined wastes incinerated and 50% landfilled.

i) Not applicable.

j) Totals may not add due to rounding.

Table B.3 Vapor Phase Chlorination of 1,1-Dichloroethane

	Product Stream, Mole %	
Reaction Product	Process A[a]	Process B[b]
Vinyl Chloride	22.7	19
1,1-Dichloroethane	4.6	38
1,1-Dichloroethene	34.9	6
1,1,1-Trichloroethane	25.9	36
1,1,2-Trichloroethane	1.1	1.5
cis-1,2-Dichloroethene	2.7	0.5
trans-1,2-Dichloroethene	2.3	0.5
Tetrachloroethane	1.5	--
Trichloroethene	2.9	--
Tetrachloroethene	0.2	--
Pentachloroethane	0.1	--
Unknown	1.2	--

a) Tubular nickel reactor 6.1 m x 6.35 mm ID. Reactor conditions: 450°C, 3.55 atm., 1 sec. residence time, molar ratio Cl_2/1,1-dichloroethane: 0.7, 1,300 ppm CO_2 added to gaseous feed. Source: Rideout and Monsell, 1980.

b) Glass reactor 0.75 m x 50 mm ID. Reactor conditions: 410°C, 1 atm., 8 sec. residence time, molar ratio Cl_2/1,1-dichloroethane: 0.45. Source: Campbell and Carruthers, 1972.

Table B.4 Industrial Classes Utilizing Degreasing

Source Type	SIC
Industrial degreasing	
Metal furniture	25
Primary metals	33
Fabricated products	34
Nonelectric machinery	35
Electric equipment	36
Transportation equipment	37
Instruments and clocks	38
Miscellaneous	39
Automotive[a]	
Auto repair shops and garages	75
Automotive dealers	55
Gasoline stations	55
Maintenance shops	a
Textile plants (fabric scouring)	22

a) No applicable SIC for this category.

Source: EPA, 1979c.

Table B.5 Industrial Wastewaters in which 1,1,1-Trichloroethane Has Been Detected

Industry	Number of Times Detected	Number of Samples Taken
Adhesives/Sealants	1	11
Batteries	1	3
Coal Coating	2	12
Coal Mining	18	249
Electrical	9	35
Electroplating	3	18
Foundries	3	54
Iron/Steel	1	431
Laundries	8	56
Leather	3	81
Mechanical Products	26	35
Nonferrous Metals	3	173
Organic Chemicals	4	b
Organics/Plastics	122	723
Paint/Ink	45	94
Pesticides	10	147
Petroleum Refining	7	76
Pharmaceuticals	18	95
Phosphates	1	33
Photographic	7	25
POTWs	12	40
Printing/Publishing	12	109
Pulp/Paper	4	98
Rubber	7	67
Steam/Electric	11	84
Textiles	1	121
Timber	1	285

a) False positives are accepted.
b) Not given.

Source: EPA, 1980b.

Table B.6 Industrial Wastewaters in which 1,1,2-Trichloroethane has Been Detected

Type of Wastewater	Number of Times Detected[a]	Number of Samples Taken
Adhesives/Sealants	1	11
Foundries	1	34
Iron/Steel	2	431
Laundries	2	56
Mechanical Products	7	35
Organics/Plastics	22	723
Paint/Ink	8	94
Petroleum Refining	7	76
Pharmaceuticals	4	95
Phosphates	1	33
Printing/Publishing	1	109
Timber	1	285

a) False positives are accepted

Source: EPA, 1980b.

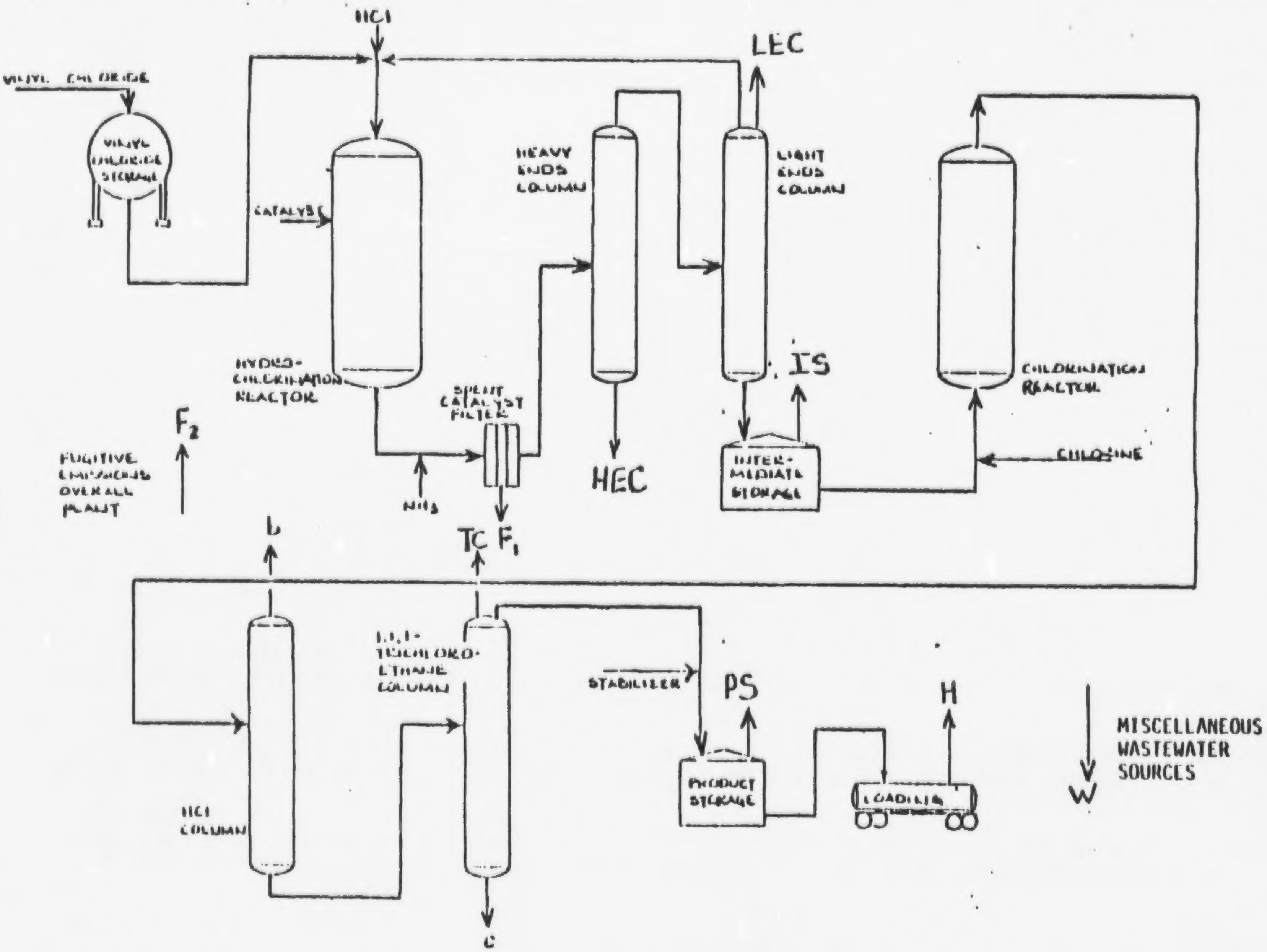
HCl
VINYL CHLORIDE
VINYL CHLORIDE STORAGE
CATALYST
HYDRO-CHLORINATION REACTOR
NH3
SPENT CATALYST FILTER
TC F1
HEAVY ENDS COLUMN
HEC
LEC
LIGHT ENDS COLUMN
IS
INTER-MEDIATE STORAGE
CHLORINATION REACTOR
CHLORINE
F2
FUGITIVE EMISSIONS OVERALL PLANT
b
HCl COLUMN
1,1,1-TRICHLORO-ETHANE COLUMN
c
STABILIZER
PS
PRODUCT STORAGE
H
LOADING
MISCELLANEOUS WASTEWATER SOURCES
W

Figure B.1 Flow Diagram for 1,1,1-Trichoroethane Production from Vinyl Chloride and Point and Nonpoint Waste Sources[a]

footnotes, next page

Figure B.1 (concluded)

a) F_2=Fugitive Emissions; TC=1,1,1-Trichloroethane Column Vent; F_1=Filter; HEC=Heavy Ends Column Vent; LEC=Light Ends Column Vent; IS=Intermediate Storage; PS-Product Storage; H=Handling; and W=Miscellaneous Wastewaters.

b) This stream is primarily composed of hydrogen chloride gas and low-boiling organic compounds and is either used to supply the hydrogen chloride requirements of other chlorinated organic processes directly or is purified and then used.

c) This bottom stream is composed primarily of 1,1,2-trichloroethane, which is kept in-house as a feed material to other chlorinated organic processes.

Source: EPA, 1979a and 1979b.

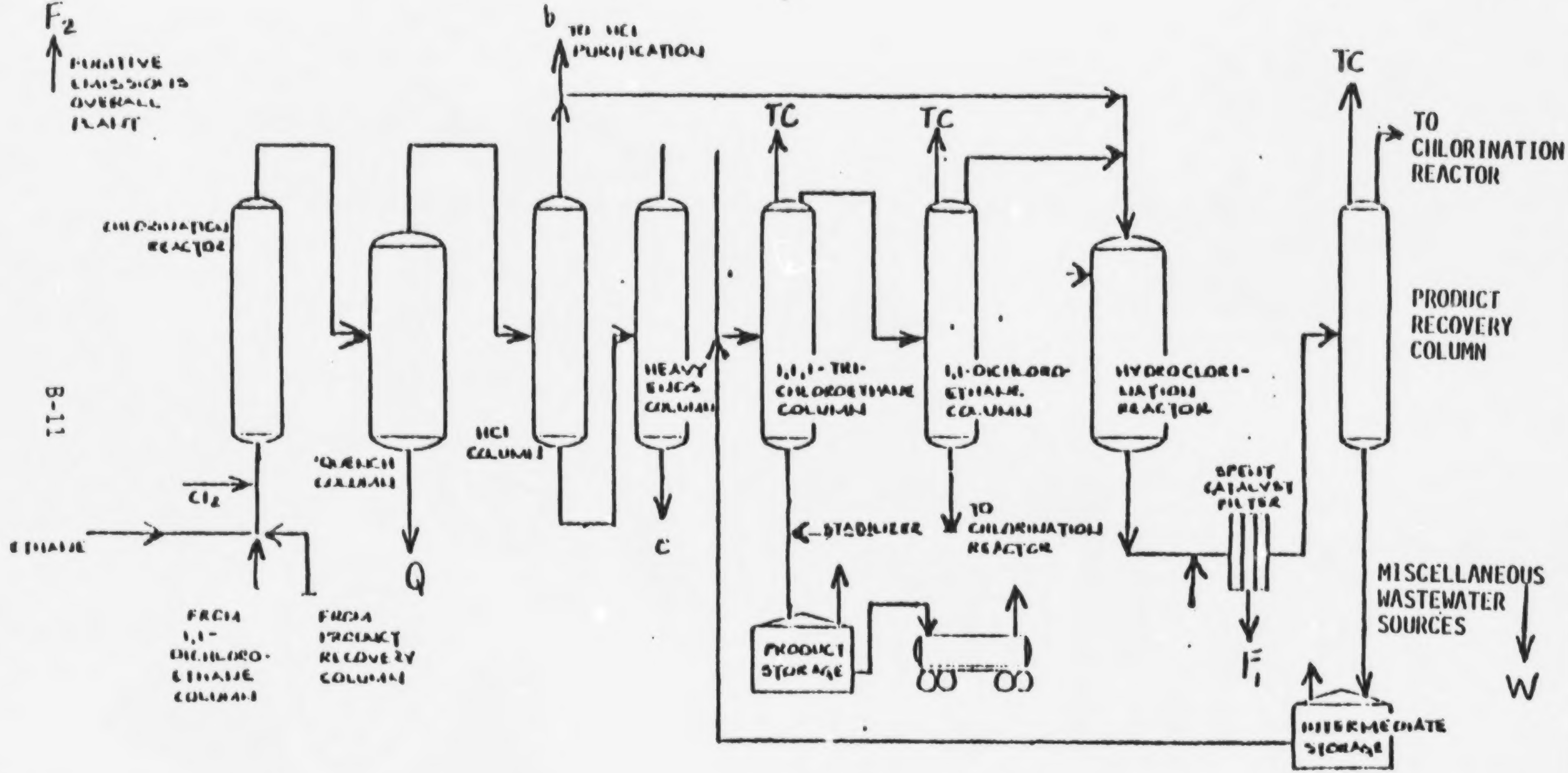
F2
FUGITIVE EMISSIONS OVERALL PLANT
b TO HCl PURIFICATION
TC
TC
TC
TO CHLORINATION REACTOR
CHLORINATION REACTOR
QUENCH COLUMN
HCl COLUMN
HEAVY ENDS COLUMN
1,1,1-TRICHLOROETHANE COLUMN
1,1-DICHLOROETHANE COLUMN
HYDROCLORINATION REACTOR
PRODUCT RECOVERY COLUMN
Cl2
ETHANE
Q
C
FROM 1,1-DICHLOROETHANE COLUMN
FROM PRODUCT RECOVERY COLUMN
STABILIZER
TO CHLORINATION REACTOR
SPENT CATALYST FILTER
F1
PRODUCT STORAGE
INTERMEDIATE STORAGE
MISCELLANEOUS WASTEWATER SOURCES
W

Figure B.2 Flow Diagram for 1,1,1-Trichloroethane Production from Ethane and Point and Nonpoint Waste Sources[a]

a) F_2=Fugitive emissions; Q=quench column vent; TC=1,1,1-trichloroethane column, 1,1-dichloroethane column and product recovery column vents combined; F_1=filter (catalyst) vent; RS=recycle storage vent; PS=product storage vent; H=handling; and W=wastewaters from steam stripping.

b) Wastes from the hydrogen chloride column overhead stream contains HCl, ethane and ethylene.

c) Wastes in this bottoms stream (primarily 1,2-dichloroethane and 1,1,2-trichloroethane) are transferred as feed to other chlorinated hydrocarbon processes.

Source: EPA, 1979a and 1979b.

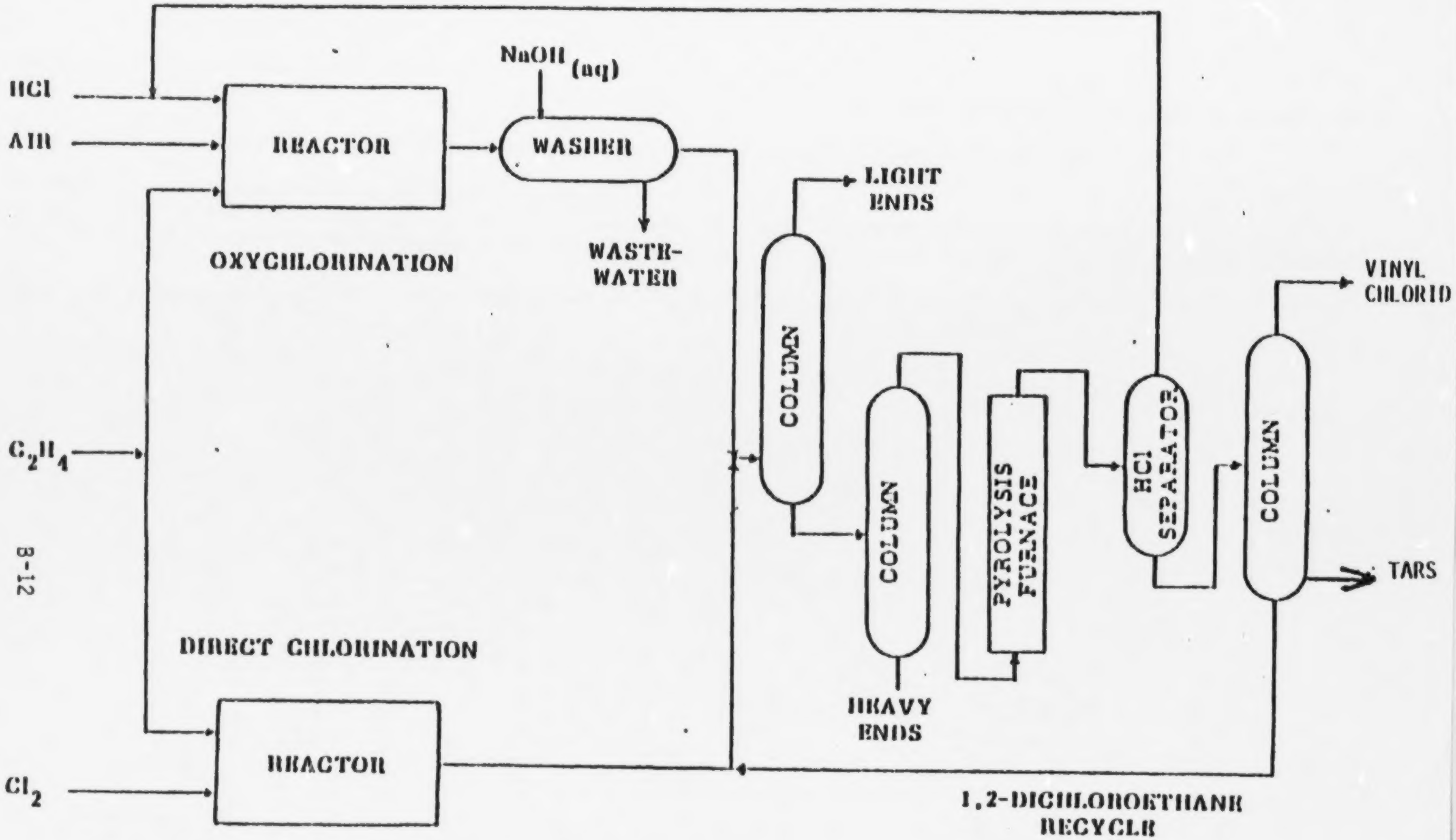
HCl
AIR
REACTOR
NaOH (aq)
WASHER
WASTE-WATER
OXYCHLORINATION
LIGHT ENDS
COLUMN
COLUMN
HEAVY ENDS
PYROLYSIS FURNACE
HCl SEPARATOR
COLUMN
VINYL CHLORID
TARS
C2H4
DIRECT CHLORINATION
Cl2
REACTOR
1,2-DICHLOROETHANE RECYCLE

Figure B.3 The Balanced Process for Vinyl Chloride Manufacture and Waste Sources

Source: EPA, 1979d.

APPENDIX C

SOLVENT RECYCLE CALCULATIONS

Derivations of the total quantity of solvent used 1979, including the amount recycled from the previous year is shown below; Table C1 gives values used to derive variable y.

Quantity Recycled = $x \cdot$ quantity wasted $\quad x = .45$ (45% of waste is recycled)

Quantity Used = quantity virgin solvent + quantity recycled or
used = virgin solvent + .45 waste.

Quantity Wasted = $y \cdot$ quantity used or y (virgin solvent + .45 waste)

$$y = \text{percent wasted solvent } \frac{68{,}630}{220{,}130} = .312$$

Solving for waste:

Waste = y (virgin solvent) + .45 y waste
waste = 0.363 (virgin solvent)

Then:

Recycle = .45 waste
= (.45) (.363) (virgin solvent)
=0.162 virgin solvent

Also: Use = Virgin solvent + recycle
Use - 0.1404 Use = virgin solvent
Use = 1.16 (virgin solvent)

Table C.1 Waste Solvent Generation by Degreasing Operation

Operation	Virgin Solvent Used (kkg)	Precent (%) Solvent Wasted	Solvent Wasted (kkg)
Cold Cleaning:			
Manufacturing	23,310	40-60(50)	11,660
Maintenance	29,700	50-75(62.5)	18,560
Open-top vapor degreasing	106,280	20-25(22.5)	23,910
Conveyorized vapor degreasing	45,530	10-20(15)	6,830
Conveyorized nonboiling degreasing	12,070	40-60(50)	6,040
Fabric scouring	3,260	40-60(50)	1,630
Total[a]	220,130		68,630

a) Totals do not add due to rounding.

APPENDIX C

AMBIENT LEVELS OF 1,1,1-TRICHLOROETHANE

The compound 1,1,1-trichloroethane has been found in a broad range of environmental media such as: freshwaters, saltwaters, soils, sediments, and the atmosphere (Table C1). The concentration of 1,1,1-trichloroethane in these media depends upon many factors (i.e., location of sampling site and meteorological conditions).

According to Singh and his associates (1977), 1,1,1-trichloroethane is present in the environment due to the activities of mankind and has no known natural source. Furthermore, the urban-rural relationship of 1,1,1-trichloroethane is typical of an urban-sourced pollutant (Table C1), and in fact, the average concentration ratio of the species in urban and rural air is about 15 (Singh et al. 1977). Consequently, 1,1,1-trichloroethane wastes found in the environment are most likely released from man's activities.

Table C.2 Concentrations of 1,1,1-Trichloroethane in Select Environmental Samples

Environmental Media	Sample Location[a] U	R	Mean Concentration (ppt)	Information Source
Freshwater Influent to POTW[b]	✓		16,500	EPA, 1976
Freshwater Influent to POTW[b]	✓		16,500	Sellar, Lichtenberg, and Kroner, 1974
Tap Water	✓		22,000	EPA, 1977c
Surface Water (lake)		✓	50	EPA, 1977c
Seawater (coastal)		✓	140	Singh, Salas, and Cavanagh, 1977
Soil		✓	630	EPA, 1977c
Sediments (lake)		✓	430	EPA, 1977c
Air		✓	84	Singh, Salas, and Cavanagh, 1977
Air	✓		830	Lillian, *et. al*., 1976
Air		✓	100(±15)	Grimsrud and Rassmussen, 1975
Air		✓	~<300	EPA, 1977c
Air	✓		610	Lillian, *et. al*., 1975
Air	✓		1,590	Lillian, *et. al*., 1975
Air		✓	67	Lillian, *et. al*., 1975
Air		✓	95	Russell and Shadoff, 1977
Air		✓	83	Russell and Shadoff, 1977

a) U = Urban; R = Rural.

b) Before Treatment

APPENDIX D

D.1 ESTIMATION OF VOLATILIZATION FROM WATER

Volatilization from water can be estimated using procedures described in the literature. The mathematical modeling of volatilization involves interphase exchange coefficients that depend on the chemical and physical properties of the chemical in question, the presence of other pollutants, and the physical properties of the water body and atmosphere above it. Basic factors controlling volatilization are solubility, molecular weight, and the vapor pressure of the chemical and the nature of the air-water interface through which the chemical must pass.

Volatilization estimates can be based on available laboratory and environmental data. Because of the lack of data for most chemicals, however, estimates of volatilization rates from surface waters on the basis of mathematical data and laboratory measurements are necessarily of unknown precision. Still, comparisons of experimental results with theoretical predictions indicate that these predictive techniques generally agree with actual processes within a factor of two or three in most cases.

The methods described below have been used to estimate volatilization from natural surface water (see Section 4.12). The EXAMS Model has been used to investigate behavior in natural surface water bodies, however, this method was not used as input to EXAMS. An input parameter similar to the reaeration coefficients described below is used in EXAMS to estimate volatilization; this value was obtained elsewhere.

The following procedures can be used to estimate the volatilization rate of a chemical. Minimum data required are:

- Chemical properties--vapor pressure, aqueous solubility, molecular weight;
- Environmental characteristics--wind speed, current speed, depth of water body;

(1) Find or estimate the Henry's Law constant H from:

$$H = P/S \quad \text{atm-m}^3/\text{mole} \tag{1}$$

where P = vapor pressure, atm
S = aqueous solubility, mole/m^3.

When calculating H as a ratio of vapor pressure to solubility, it is essential to have these data at about the same temperature and applicable to the same physical state of the compound. Data for pure compounds should be used because vapor pressure and solubilities of mixtures may be suspect.

(2) If $H<3 \times 10^{-7}$ atm-m^3/mole, volatilization can be considered unimportant as an intermedia transfer mechanism and no further calculations are necessary.

(3) If $H>3 \times 10^{-7}$ atm-m^3/mole, the chemical can be considered volatile. The nondimensional Henry's Law constant H' should be determined from:

$$H' = H/RT \tag{2}$$

where R = gas constant, 8.2×10^{-5} atm-m^3/mole K

T = temperature, K.

At 20C (293K) RT is 2.4×10^{-2} atm-m^3/mole.

(4) The liquid phase exchange coefficient k_ℓ must be estimated. This coefficient is from a method that analyzes the volatilization process on the basis of a two-layer film, one water and one air, which separates the bulk of the water body from the bulk of the air (Liss and Slater 1974).

For a low molecular weight compound ($15<M<65$),

$$k_\ell = \sqrt{44/M} \quad \text{cm/hr} \tag{3}$$

where M = molecular weight of the chemical.

If $M>65$, k_ℓ can be estimated from equations developed by Southworth (1979). Because this method is different from Equation (3), the estimated values may vary. If the average wind speed is ≤ 1.9 m/sec,

$$k_\ell = \left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right) \sqrt{\frac{32}{M}} \tag{4}$$

where V_{curr} = water current velocity, m/sec

Z = depth of water body, m.

If wind speed is >1.9 m/sec and <5 m/sec,

$$k_\ell = \left(\frac{V_{curr}^{0.969}}{Z^{0.673}}\right) \sqrt{\frac{32}{M}} \; e^{0.526\,(V_{wind}-1.9)} \quad \text{cm/hr} \tag{5}$$

where V_{wind} = windspeed, m/sec.

If wind speed is >5 m/sec, liquid phase exchange coefficients are difficult to predict and may range up to 70 cm/hr.

(5) The gas phase exchange coefficient must be estimated. This too is based on the two-film analysis. For a compound of $15<M<65$ (Liss and

Slater (1974),

$$k_g = 3000\sqrt{18/M} \text{ cm/hr} \qquad (6)$$

If M>65 (Southworth 1979),

$$k_g = 1137.5\ (V_{wind} + V_{curr})\sqrt{18/M} \text{ cm/hr}\ . \qquad (7)$$

(6) The Henry's Law constant and gas and liquid phase exchange coefficients are used to compute the overall liquid phase mass transfer coefficient, K_L (Liss and Slater 1974), which is an indicator of the volatilization rate:

$$K_L = \frac{(H/RT)k_g k_\ell}{(H/RT)k_g + k_\ell} = \frac{H'k_g k_\ell}{H'k_g + k_\ell} \text{ cm/hr} \qquad (8)$$

(7) The volatilization rate constant k_v is:

$$k_v = K_L/Z \text{ hr}^{-1} \qquad (9)$$

where Z is in cm.

(8) Assuming a first order volatilization process, the concentration in the stream in the absence of continuing inputs at the location at which volatilization occurs, is

$$c(t) = c_o e^{-k_v t} \qquad (10)$$

where $c(t)$ = pollutant concentration in the water column at time t

c_o = initial pollutant concentration in the water column.

(9) The half-life in the water column for the pollutant volatilizing at a first order rate is:

$$\tau_{\frac{1}{2}} = \frac{0.69\ Z}{K_L} \text{ hr.} \qquad (11)$$

Another method for computing k_v for highly volatile chemicals with $H>10^{-3}$ atm-m^3/mole is based on reaeration rate coefficients (Smith and Bomberger 1977, Smith et al. 1979, Tsivoglou 1967). The following data are required:

- Ratio of reaeration rate of chemical to that of water,
- Reaeration rate of oxygen for water bodies in the environment or steamflow parameters (velocity, stream bed slope, depth).

If the oxygen reaeration rate is known for a given water body or type of water body, the volatilization rate constant for the pollutant can be estimated from (Smith and Bomberger 1979):

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab}\,(k_v^o)_{env} \qquad (12)$$

where k_v^c = first order volatilization rate constant for the particular chemical (hr^{-1});

k_v^o = reaeration rate constant for oxygen (hr^{-1});

env = designates values applicable to environmental situations;

lab = designates laboratory measured values.

This equation applies particularly to rivers. For lakes and ponds, the following equation may be more accurate:

$$(k_v^c)_{env} = (k_v^c/k_v^o)^{1.6}_{lab}\,(k_v^o)_{env} \qquad (13)$$

Typical values of $(k_v^o)_{env}$ are given in the literature and reported by Smith et al (1979):

Water Body	$(k_v^o)_{env}$, hr^{-1}
Pond	0.0046 - 0.0096
River	0.008, 0.04 - 0.39
Lake	0.004 - 0.013

The values for ponds and lakes are speculative and depend on depth.

Mackay and Yuen (1979) present the equations listed below that correlate k_v^o with river flow velocity, depth, and slope:

Tsivoglou-Wallace: $k_v^o = 638\, V_{curr} s \; hr^{-1}$ (14)

Parkhurst-Pomeroy: $k_v^o = 1.08\,(1 + 0.17\,F^2)\,(V_{curr} s)^{0.0375}\; hr^{-1}$ (15)

Churchill et al.: $k_v^o = 0.00102 V_{curr}^{2.695}\, Z^{-3.085}\, s^{-0.823}\; hr^{-1}$ (16)

If no slope data are available:

Isaccs-Gundy: $k_v^o = 0.223 V_{curr} Z^{-1.5}\; hr^{-1}$ (17)

Langbein-Durum: $k_v^o = 0.241\, V_{curr} Z^{-1.33}\; hr^{-1}$ (18)

where V_{curr} = river flow velocity (m/s);

s = river bed slope = m drop/m run (nondimensional);

Z = river depth (m);

g = acceleration of gravity = 9.8 m/s^2.

Because none of the foregoing is clearly superior to the others, the best approach is probably to use all that are applicable and then average the results. For a river 2 m deep, flowing at 1 m/sec, the reaeration rate is estimated as 0.042/hr. $(k_v^c/k_v^o)_{lab}$ is known for some chemicals (See Table D.1). If a $(k_v^c/k_v^o)_{lab}$ value is not known, one for a similar high-volatility chemical should be a reasonable substitute.

In principle, k_v^c is the same as (K_L/Z); however, due to the use of $(k_v^o)_{env}$, k_v^c has the depth and other water body characteristics embedded within it. Therefore, no adjustment is required for use in the first order volatilization equation.

D.2 ESTIMATION OF VOLATILIZATION RATE FOR TRICHLOROETHANES

The half-lives for trichloroethanes at 20°C in a river 1 meter deep flowing at 1 m/s will be estimated. Wind speed is 3 m/sec.

D.2.1 1,1,1-Trichloroethane

Vapor pressure of 1,1,1-trichloroethane at 20°C is 100 mm Hg (0.13 atm), molecular weight is 133.4 g/mole, and solubility is 4400 mg/ℓ (33 mole/m^3) at 20°C (Verschueren 1977).

1. Calculate the Henry's Law constant:

$$H = \frac{0.13 \text{ atm}}{33 \text{ moles/m}^3} = 0.0039 \text{ atm-m}^3\text{/mole}$$

2. Because $H > 10^{-3}$ atm-m^3/mole, 1,1,1-trichloroethane is highly volatile.

3. The nondimensional Henry's Law constant is H/RT,

$$H' = 0.0039/0.024 = 0.16 \text{ at } 20°\text{C}.$$

4. Because $M > 65$ and $V_{wind} > 1.9$ m/sec, the liquid phase exchange coefficient k_ℓ is:

$$k_\ell = 23.51\ (1^{0.969}/1^{0.673})\sqrt{32/133.4}\ e^{.526(3-1.9)} = 20.5 \text{ cm/hr.}$$

5. The gas phase exchange constant is:

$$k_g = 1137.5\ (3+1)\sqrt{18/133.4} = 1700 \text{ cm/hr.}$$

TABLE D.1

MEASURED REAERATION COEFFICIENT RATIOS FOR HIGH VOLATILITY COMPOUNDS

Compound	H atm-m^3/ mole	Measured k_v^c/k_v^o
Chloroform	3.8×10^{-3}	.57 ± .02 .66 ± .11
1,1-Dichloroethane	5.8×10^{-3}	.71 ± .11
Oxygen	7.2×10^{-2}	1.0
Benzo [b] thiophene	2.7×10^{-4}	.38 ± .08
Dibenzothiophene	4.4×10^{-4}	.14
Benzene	5.5×10^{-3}	.57 ± .02
Carbon dioxide		.89 ± .03
Carbon tetrachloride	2.3×10^{-2}	.63 ± .07
Dicyclopentadiene		.54 ± .02
Ethylene	8.6	.87 ± .02
Krypton		.82 ± .08
Propane		.72 ± .01
Radon		.70 ± .08
Tetrachloroethyene	8.3×10^{-3}	.52 ± .09
Trichloroethylene	1×10^{-2}	.57 ± .15

Source: Smith *et al*. (1979).

6. The overall liquid phase exchange coefficient is:

$$K_L = \frac{(0.16)(1700)(20.5)}{(0.16)(1700)+(20.5)} = 19 \text{ cm/hr.}$$

7. The volatilization rate constant is:

$$k_v = 19/100 = .19 \text{ hr.}$$

8. The half-life for volatilization is:

$$\tau_{1/2} = 0.69/0.19 = 3.6 \text{ hr.}$$

Alternatively, by the reaeration coefficient method:

1. The reaeration rate constant can be estimated by equations (17) and (18):

$$(k_v^o)_{env} = 0.223\ (1)(1)^{-1.5} = 0.223/\text{hr},$$

$$(k_v^o)_{env} = 0.241\ (1)(1)^{-1.33} = 0.241/\text{hr.}$$

The average of these values is about 0.23/hr. This is within the range listed in the table of reaeration rates (0.008 - 0.39/hr for rivers).

2. A laboratory measured value of k_v^c/k_v^o is not available for 1,1,1-trichloroethane. Using the k_v^c/k_v^o value from Table D.1 for a chemical with a similar H, chloroform ($H = 3.8 \times 10^{-3}$),

$$(k_v^c)_{env} = (0.62)(0.23) = 0.14/\text{hr.}$$

For comparison, the rate constant corresponding to the value of K_L estimated above is 0.19/hr.

3. Using equation (11), the half-life is:

$$\tau_{1/2} = 0.69/(k_v^c)_{env} = 0.69/0.14 = 4.9 \text{ hr.}$$

This agrees fairly well with the 3.6 hr estimated by the preceding method. In either case, volatilization is rapid.

D.2.2 1,1,2-Trichloroethane

Vapor pressure of 1,1,2-trichloroethane at 20°C is 19 mm Hg (.025 atm), molecular weight is 133.4 gm/mole, and solubility is 4500 mg/ℓ (33.7 mole/m^3) at 20°C (Verschureren 1977).

1. Calculate the Henry's Law constant:

$$H = \frac{0.025 \text{ atm}}{33.7 \text{ mole/m}^3} = 7.4 \times 10^{-4} \text{ atm-m}^3\text{/mole.}$$

2. Because $H > 3 \times 10^{-7}$ but $< 10^{-3}$, 1,1,2-trichloroethane is only moderately volatile.

3. The nondimensional Henry's law constant is H/RT,

$H' = 7.4 \times 10^{-4}/0.024 = 3.1 \times 10^{-2}$.

4,5. k_ℓ and k_g are the same as for 1,1,1-trichloroethane because molecular weights are equal:

k_ℓ = 20.5 cm/hr

k_g = 1700 cm/hr.

6. The overall liquid phase exchange constant is:

$$K_L = \frac{(3.1 \times 10^{-2})(1700)(20.5)}{(3.1 \times 10^{-2})(1700) + 20.5} \approx 15 \text{ cm/hr.}$$

7. The volatilization rate constant is:

k_v = 15/100 = 0.15/hr.

8. The half-life for volatilization is:

$\tau_{1/2}$ = 0.69/0.15 = 4.6 hr.

Because 1,1,2-trichloroethane is not highly volatile, the reaeration coefficient method is not used to estimate volatility.

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APPENDIX E

ATMOSPHERIC FATE OF TRICHLOROETHANES

There must be a mechanism for removal of 1,1,1-trichloroethane from the atmosphere since cumulative world production (and assumed emissions) up to December 1975 uniformly mixed in the atmosphere would yield atmospheric levels about 75% higher than concentrations actually measured (Singh et al. 1977). This appendix discusses removal mechanisms for the trichloroethanes, although most information relates to 1,1,1-trichloroethane.

The compound 1,1,1-trichloroethane is resistant to photo-oxidation (Hanst 1978). In the laboratory, no decay occurred when the compound was irradiated with black light-blue lamps in the presence of 500 pphm NO_2 and 50% relative humidity (Lillian et al. 1975). Less than 5% decomposition was noted in 23.5 hr when 1,1,1-trichloroethane at 10 ppm* and NO at 5 ppm was irradiated by a lamp with a UV short wavelength cutoff at 290 nm. Less than 5% decomposition was noted in 28 days at 50 ppm 1,1,1 trichloroethane and 10 ppm NO_2 (Dilling et al. 1975). In studies with about 25 times the chlorine required to initiate photo-oxidation in the chlorinated ethanes in comparable times, the following reaction products were noted: CO, HCl, CCl_2O (phosgene), and CO_2. Phosgene was found to be the only chlorine-containing product, comprising 50% of the 1,1,1-isomer consumed. The 1,1,1-isomer was found to be the least reactive of the chlorinated ethanes, some 30-50 times less reactive than 1,1,2-trichloroethane. The 1,1,2-isomer photo-oxidized rather rapidly, forming formyl chloride (HCClO), phosgene (CCl_2O), and chloroacetyl chloride (CCl_2HCOCl). Formyl chloride accounted for 44% of the chemical consumed (Spence and Hanst 1973).

The rate of photo-oxidation is a function of latitude since OH concentration ([OH]) is a function of latitude. Altshuller (1980) estimates that at 40°N latitude it would take 177 days in January and 11 days in July for 1% of atmospheric 1,1,1-trichloroethane to be consumed by OH.

Because of 1,1,1-trichloroethane's long atmospheric lifetime and pervasive use, it is distributed worldwide even though an estimated 97% of the world's use occurs in the Northern Hemisphere (Neely and Agin 1980). The compound exists long enough for a portion to be transported into the stratosphere. Lifetime in the atmosphere has been estimated to be between 1.1 years and 15 years with 6-10 years a reasonable "average" estimate (Hanst 1978, Cox et al. 1976, Singh et al. 1978, Altshuller 1980, Rowland 1980, Neely and Agin 1980, Singh et al. 1980, and Campbell 1980).

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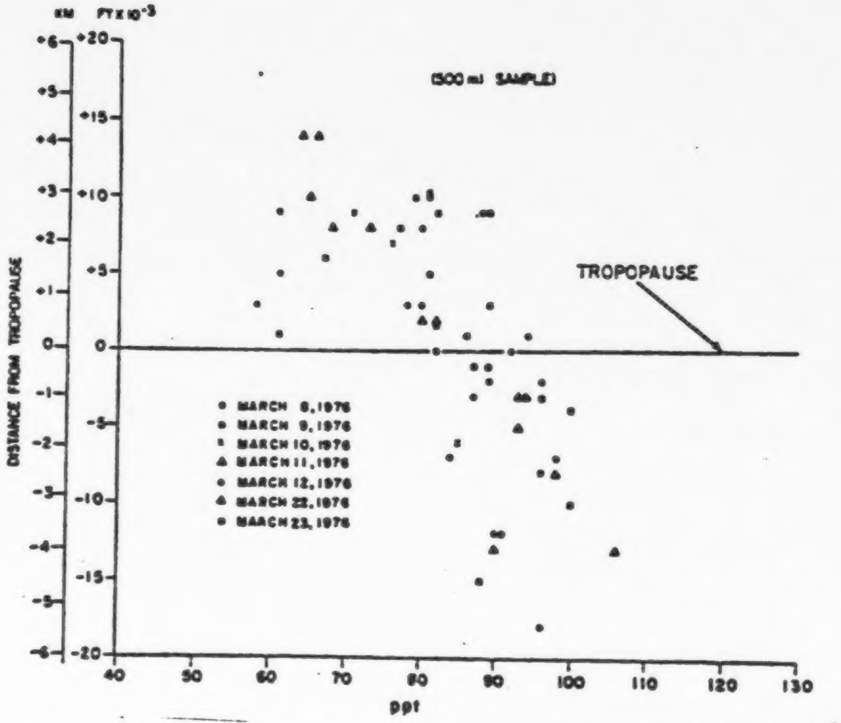
*Concentrations were originally reported in ppm, ppb, etc. Those units will be maintained in this section to facilitate comparison of concentrations. 1ppm = 5.46 mg/m^3 for 1,1,1 trichloroethane.

Concentrations vary with location, altitude, latitude, and hemisphere (Cronn *et al*. 1977, Singh *et al*. 1980, Cronn 1980, Campbell 1980, Singh *et al*. 1978, Spence and Hanst 1973). The concentration in the lower stratosphere is noticeably lower than that in the troposphere (see Figures E-1, E-2, E-3). The worldwide background in the troposphere is up to two times higher than concentrations at 13-14 km altitude, the lower reaches of the stratosphere (Spence and Hanst 1973). The transport mechanism causing this distribution is the influx of troposhperic air into the stratosphere. Daily fluctuations in the lower stratosphere are usually due to meteorologic considerations. In the intertropical convergence zone, it was noted that the rate of decline in concentrations was lower than in mid-latitude of the northern hemisphere, probably because the tropics are an area of upward transport of tropospheric air into the stratosphere (Cronn 1980).

Concentrations in the Southern Hemisphere are about 60% of concentrations in the Northern Hemisphere (Singh *et al*. 1980). In May, 1976, the (average Southern Hemisphere)/(average Northern Hemisphere) concentration ratio was 0.42 (Singh *et al*. 1978). Above 30°N, 1,1,1-trichloroethane is well mixed in the Northern Hemisphere; between 20°N and 20°S, a sharp decline is noted, and below 20°S, the concentration is lower (see Figures E-4 and E-5). This is probably due to higher OH concentrations, and hence higher removal rate around the Equator, due to amounts of sunlight and water vapor, and not to a normal mixing process. The exchange time between hemispheres is about 14-17 months (Rowland 1980, Neely and Agin 1980). Calculations indicate that one-half of all 1,1,1-trichloroethane removal occurs between 16°S and 16°N, with the rate varying with altitude. More than one-half of the removal occurs in the atmosphere below 2.4 km (Campbell 1980).

Concentrations differ between urban and rural areas. Average urban concentrations are about eight times background levels (Singh *et al*. 1978). These higher urban levels may persist for days (Cronn 1980). At times, local meteorological factors are more important than local emission patterns (Lillian *et al*. 1975). During an inversion situation in Wilmington, OH, 1,1,1-trichloroethane concentrations at 460 m, below the inversion height, were about three times higher than concentrations above 1500 m. Localized and short-term variations in concentrations in an urban area and in the plume downwind are indicative of complex variable emission patterns with a strong dependence on meteorological factors.

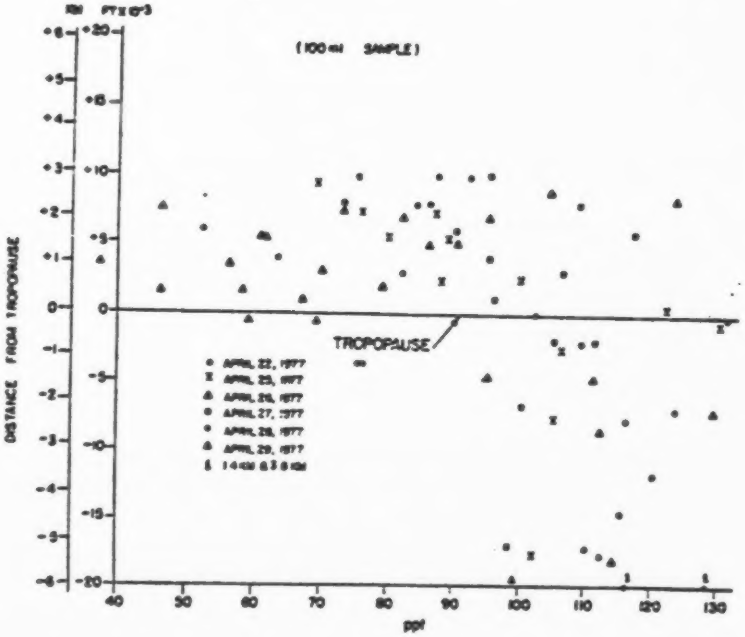
Due to a long atmospheric lifetime, 1,1,1-trichloroethane is a good tracer for the transport of urban pollutants. Figure E-6 illustrates these observations where airborne concentrations in New York City are seen to increase during the middle of the day. In the White Face Mountains of New York, concentrations are seen to increase later in the day (see Figure E-7). Relative variations and time dependence of the variations at each location reinforce the relationship between the urban and rural measurements.



Source: Cronn et al. (1976)

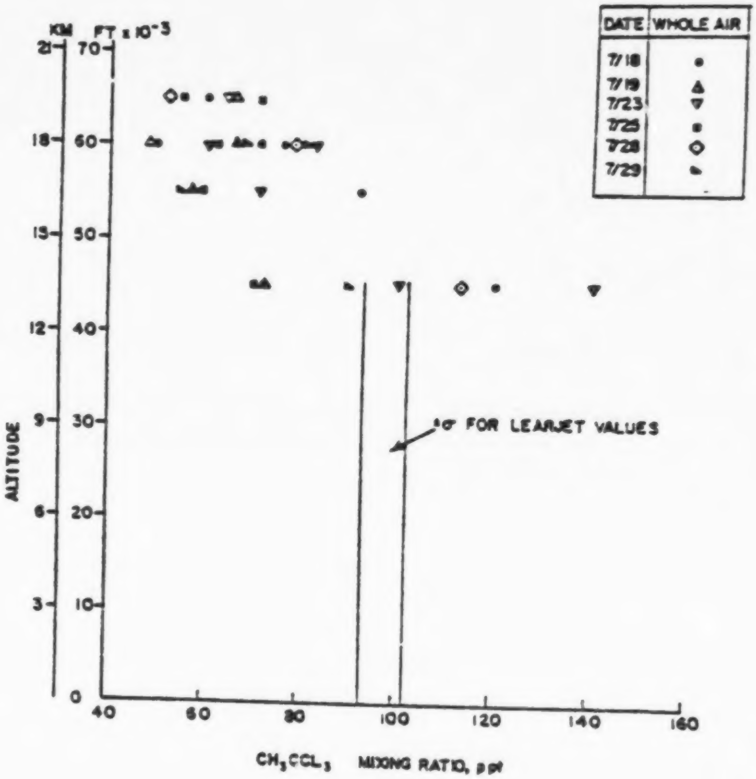
Note: 1 ppt = 5.46 ng/m^3

FIGURE E–1 MIXING RATIO DISTRIBUTION OF 1,1,1 – TRICHLOROETHANE AS A FUNCTION OF TROPOPAUSE HEIGHT, MARCH 1976, 47° N LATITUDE



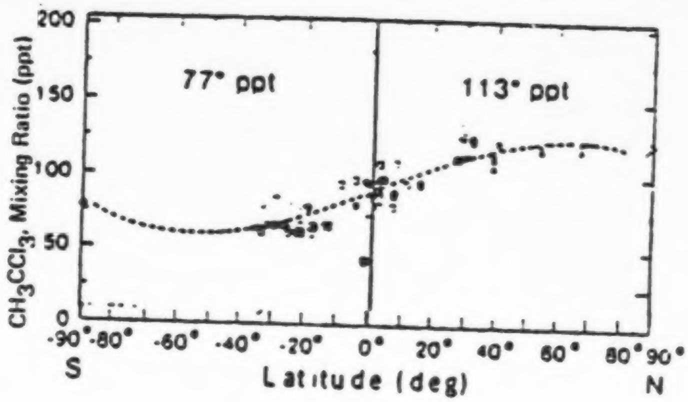
Source: Cronn et al. (1976)

FIGURE E–2 MIXING RATIO DISTRIBUTION OF 1,1,1 – TRICHLOROETHANE AS A FUNCTION OF TROPOPAUSE HEIGHT, APRIL 1977, 37° N LATITUDE



Source: Cronn and Robinson (1978)

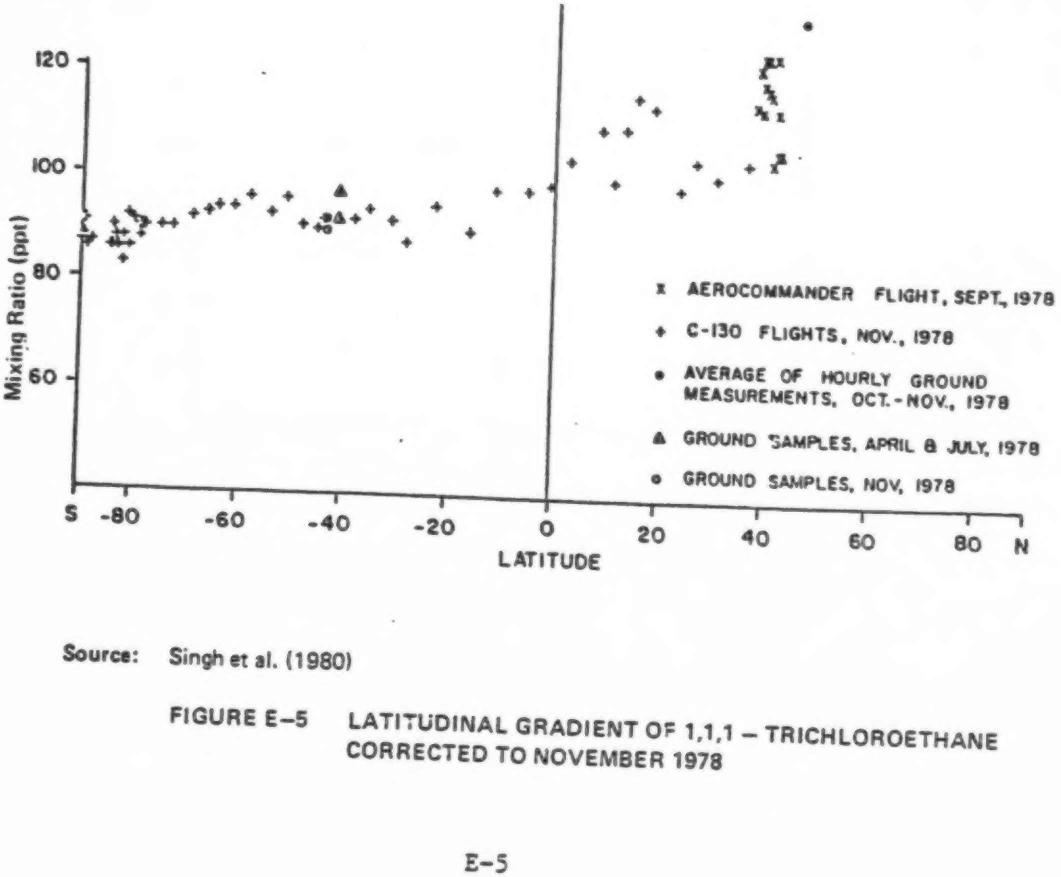
FIGURE E–3 1,1,1 – TRICHLOROETHANE MIXING RATIO DISTRIBUTION AS A FUNCTION OF TROPOPAUSE HEIGHT, JULY 1977, 9° N LATITUDE



* A weighted average concentration is used to represent the total burden of the species in the hemisphere since a significant gradient within the hemisphere is observed.

Source: Singh et al. (1980)

FIGURE E–4 GLOBAL DISTRIBUTION BY LATITUDE OF 1,1,1 – TRICHLOROETHANE IN LATE 1977



Source: Singh et al. (1980)

FIGURE E–5 LATITUDINAL GRADIENT OF 1,1,1 – TRICHLOROETHANE CORRECTED TO NOVEMBER 1978

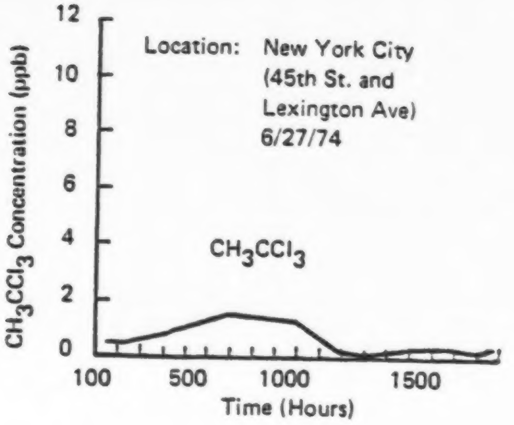


FIGURE E–6 DIURNAL VARIATIONS IN 1,1,1 – TRICHLOROETHANE LEVELS IN NEW YORK CITY

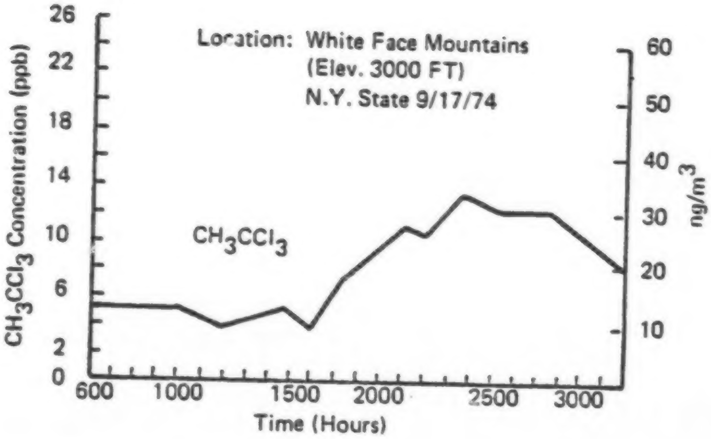


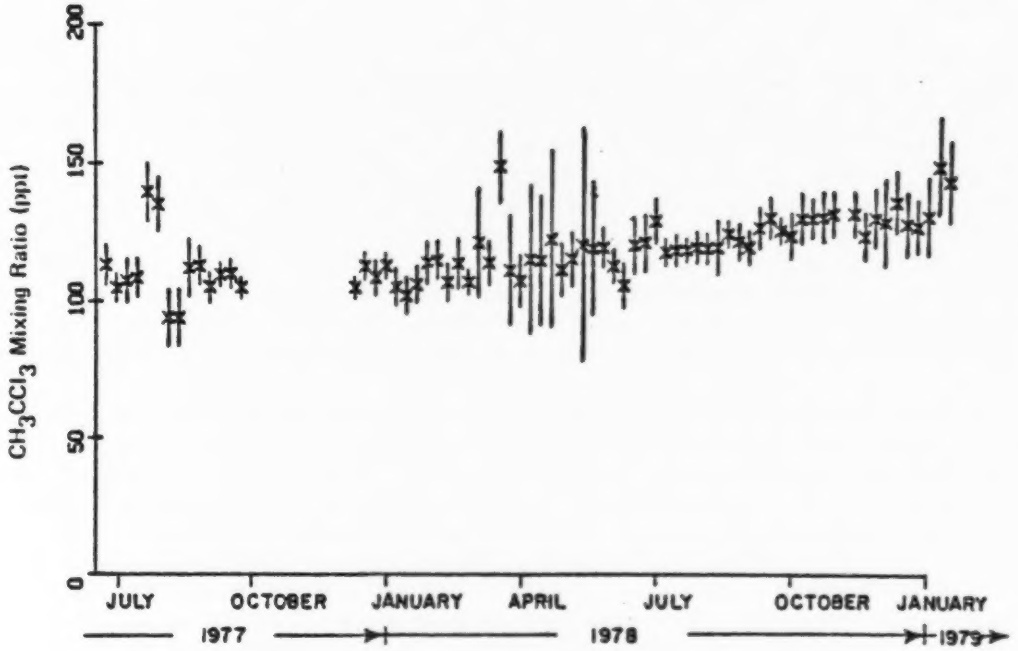
FIGURE E–7 1,1,1 – TRICHLOROETHANE LEVELS IN NON URBAN AREAS DUE TO TRANSPORT FROM URBAN AREAS

Over the past few years, atmospheric concentrations and emissions have increased (Rowland 1980). Over the 1975-77 period, concentrations in the Northern Hemisphere at temperate latitudes increased at 12-17%/yr (Singh et al. 1980, Singh et al. 1978, Singh et al. 1979), a a somewhat lower rate than expected (Singh et al. 1978). Emissions growth over the same period was also exponential (Singh et al. 1978) with available emissions data indicating about 15-25%/yr (Singh et al. 1979). On the basis of these observations, it appears that atmospheric concentrations have not increased as rapidly as emissions. Figures E-8, E-9, and E-10 show atmospheric concentrations as a function of time.

The long tropospheric lifetime of the chlorinated compound 1,1,1-trichloroethane and the past and continuing dispersive losses are of possibly serious significance (Altshuller 1980, Hanst 1978). From 12 to 25% of global 1,1,1-trichloroethane emissions may reach the stratosphere (Singh et al. 1980, Singh et al. 1979), where Cl atoms may be released by photolysis to attach and deplete ozone (Hanst 1978, Lillian et al. 1975, Altshuller 1980, Neely and Agin 1980, Singh et al. 1979, McConnell and Schiff 1978). The ozone situation can be put into perspective by comparison of 1,1,1-trichloroethane with the chlorofluoromethanes (CFM's). The annual stratospheric flux of chlorine atoms due to 1,1,1-trichloroethane is about ten times less than the flux due to Freon-11 and Freon-12 (Neely and Agin 1980). Based on several reasonable assumptions, it would take 38-55 years at a 6%/yr 1,1,1-trichloroethane growth rate to reach the present level of ozone depletion by CFM. The amount of 1,1,1-trichloroethane reaching stratospheric O_3 may be less than 6-12% of yearly emissions since in the lower stratosphere, [OH] is high enough and diffusion and mixing to the stratosphere is sufficiently slow so that more 1,1,1-trichloroethane than previously estimated (the 12-25% reported by Singh et al. 1979) may degrade due solely to tropospheric reactions before reaching the stratosphere and the O_3 layer. The steady state ozone depletion (ΔO_3) due to CFM release at 1973 levels is estimated to be 6.6-7.5% of the unperturbed value (McConnell and Schiff 1978). When 1,1,1-trichloroethane is added to the calculations, the steady state ΔO_3 is 7.8%, an increase of 20% over the 6.6% ΔO_3. If steady-state CFM levels decreased to one-half of 1973 levels, the steady-state ΔO_3 decreases to 3.3%. With a release schedule of 1,1,1-trichloroethane added (10%/year increase until 1982, then 7%/year until 1990), ΔO_3 goes to 4.6%, a 40% increase.

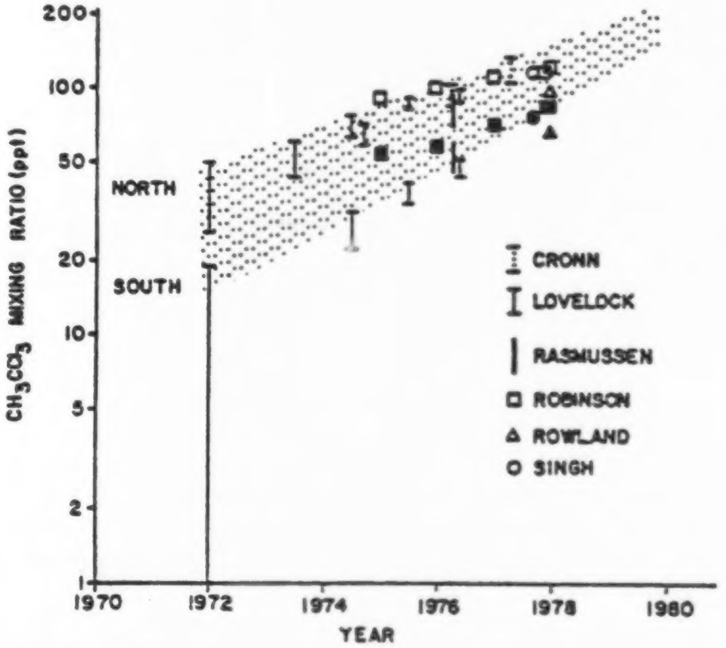
Crutzen et al. (1978) have simulated ozone depletion due to many chlorinated compounds in the atmosphere. According to their calculations, 1,1,1-trichloroethane in 1978 was contributing about 0.2% reduction in total ozone. Estimates of future ozone reductions due only to 1,1,1-trichloroethane use and release increases of 13%/year are shown in Figure E-11. Other curves for other chlorinated chemicals are also shown for comparison.

Since 1,1,1-trichloroethane has a relatively short lifetime in the atmosphere when compared with CFM's, it would contribute little to O_3 depletion 25 years after termination of emissions. This is due to the



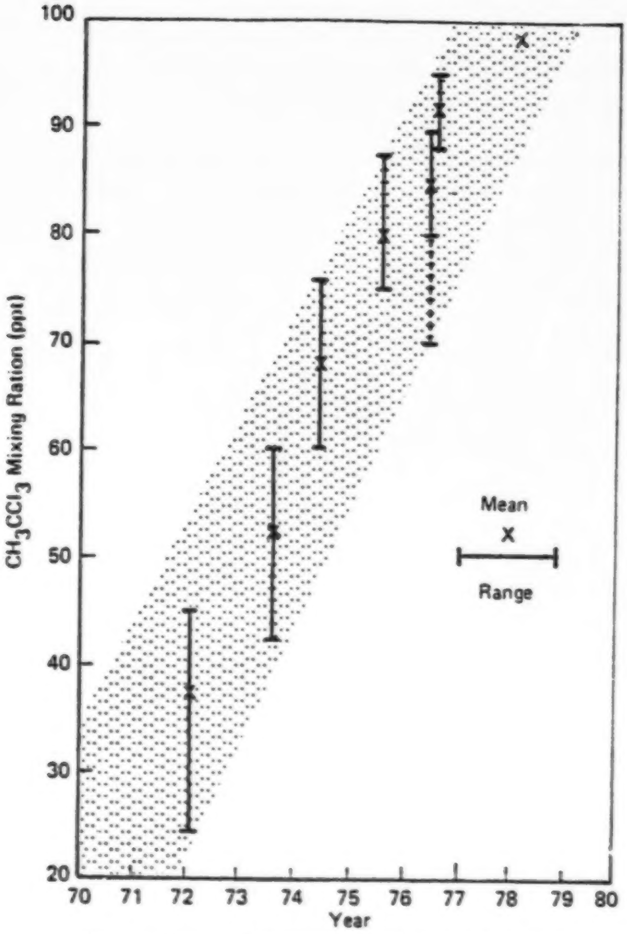
Source: Cronn (1980)

FIGURE E–8 WEEKLY AVERAGES FOR CONTINUOUS GROUND MONITORING OF 1,1,1 – TRICHLOROETHANE LEVELS, JUNE 1977 – JANUARY 1979, 47° N LATITUDE, EASTERN WASHINGTON STATE



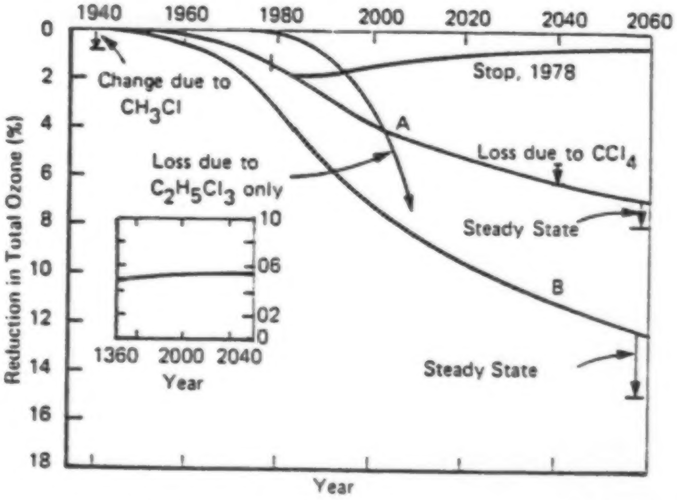
Source: Cronn (1980)

FIGURE E–9 OBSERVED NH AND SH MIXING RATIOS OF 1,1,1 – TRICHLOROETHANE LEVELS, 1972 – 1978



Source: Various data cited by Neely and Agin (1980)

FIGURE E–10 ATMOSPHERIC LEVELS OF 1,1,1 – TRICHLORETHANE, 1972 – 1978, NORTHERN HEMISPHERE



Source: Crutzen et al. (1978)

FIGURE E–11 TOTAL OZONE LOSSES FOR VARIOUS SCENARIOS tropospheric sink rather than a stratospheric sink, where most ozone is found and where Cl release is of more concern.

For the reasons discussed above, 1,1,1-trichloroethane may contribute to ozone destruction, but at a level less than that of the chlorofluoromethanes.

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